

## The Reaction of *ortho*-Substituted Aromatic Azides with Boron Trichloride or Trifluoride

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The reaction of boron trichloride or trifluoride with *ortho*-aryl, -diazoaryl, and -aryloxyaryl phenyl azides in benzene at room temperature generally gives fused azoles in high yields. Treatment of 2-nitrophenyl azide with boron trichloride mainly affords chlorinated nitroanilines, whereas with boron trifluoride it gives *N*-*o*-nitrophenylaniline. In aromatic solvents at 60 °C in the presence of boron trifluoride–diethyl ether, 2-azidobiphenyl forms carbazole and 2-(arylamino)biphenyls, the formation of which depends greatly upon the nucleophilicity of the solvent used; however, its pseudo-first-order decomposition rate is slightly greater in benzene than in toluene or *m*-xylene. Under the same conditions, phenyl azide forms diarylamines.

The results suggest that singlet nitrenium ions, arising from the corresponding azide–trihalogenoborane complexes by loss of molecular nitrogen, are generally the reactive intermediates.

Reactive species resulting from fragmentation of aryl azides, such as aryl-nitrenes and -nitrenium ions, have attracted much attention arising from synthetic, theoretical, and biological interest.<sup>1</sup> Like aryl nitrenes, aryl nitrenium ions can exist in singlet and triplet states as supported by MNDO molecular orbital prediction.<sup>2</sup> Singlet aryl nitrenium ions, generated by fragmentation of aryl azides promoted by trifluoroacetic acid (TFA) or trifluoromethanesulphonic acid (TFSA), have recently been reported to give products of aromatic *N*- and/or *C*-substitution depending upon the electronic character of substituents and reaction conditions.<sup>3,4</sup> On the other hand, regioselective aromatic *N*-substitution has been exhibited by singlet aryl nitrenium–AlCl<sub>3</sub> complexes which resulted from the decomposition of aryl azides in the presence of aluminium chloride.<sup>5</sup>

Very recently, we have reported preliminary results from a study of the reaction of various substituted phenyl azides with boron trifluoride–diethyl ether at 60 °C in methylated benzenes. These reactions lead preferentially to *N*-benzylanilines or diarylamines, the formation of which depends greatly upon the electronic nature of the phenyl azide substituent and the nucleophilicity of the aromatic solvent. Diarylamines have been ascribed to aromatic *N*-substitution by singlet nitrenium–BF<sub>3</sub> complexes, whereas *N*-benzylanilines are believed to be the products of the side-chain C–H insertion by triplet aryl nitrenium–BF<sub>3</sub> complexes.<sup>6</sup>

In this paper we report our results from a related study of the reaction of various *ortho*-substituted aryl azides (1)–(6) with boron chloride or fluoride.<sup>7</sup>

### Results and Discussion

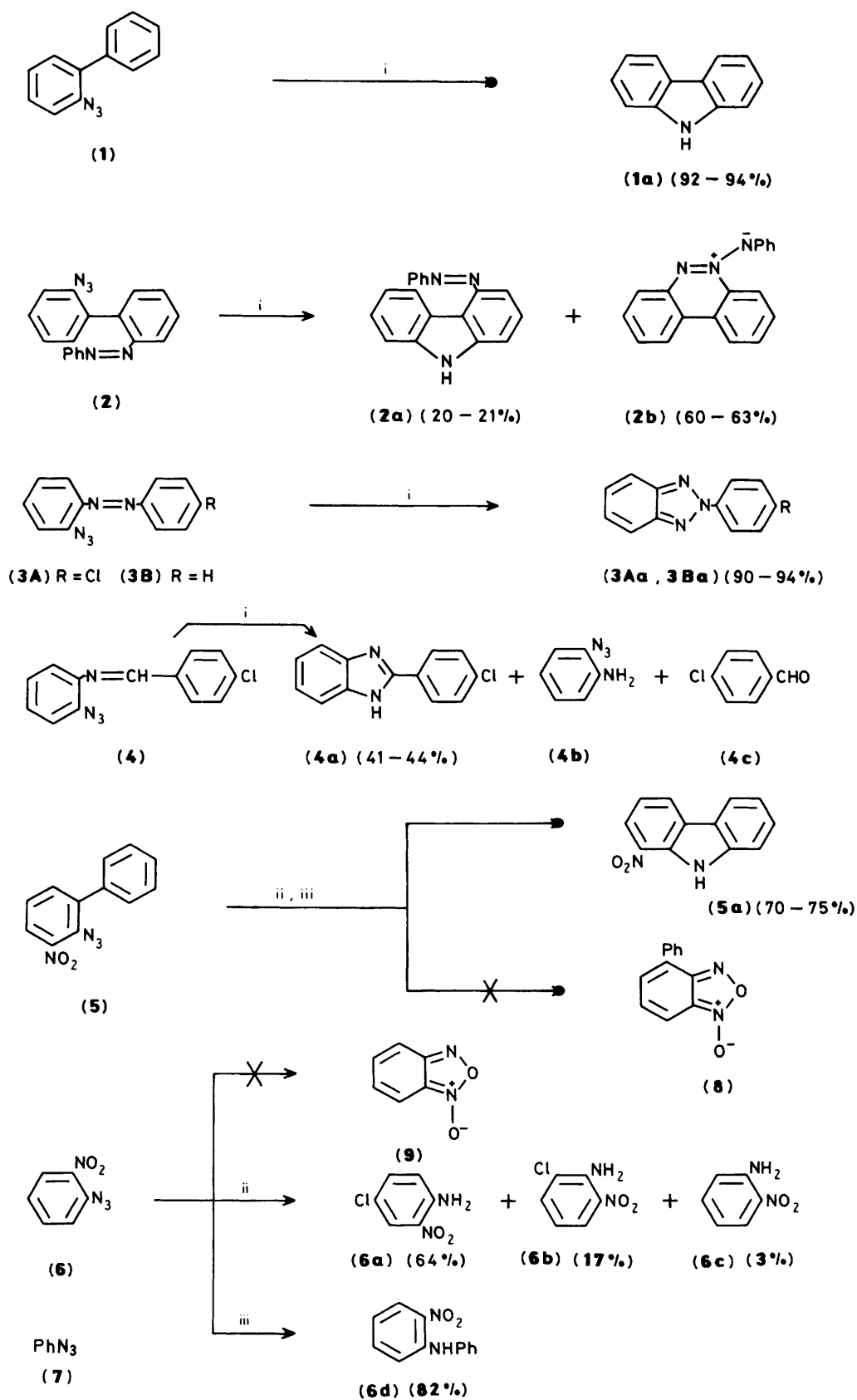
A solution of 2-azidobiphenyl (1) in benzene was treated with boron trichloride (1 mol equiv.) at room temperature. After the immediate evolution of molecular nitrogen, the reaction went to completion within *ca.* 10 min. After hydrolysis and column chromatography, carbazole (1a) was obtained in very high yield. Similar reactions of 2-azido-2'-phenylazobiphenyl (2) gave the carbazole (2a) and benzo[*c*]cinnoline *N*-phenylimide (2b) in *ca.* 1:3 molar ratio. Under the same conditions, the azides (3A) and (3B) gave almost quantitatively the corresponding benzotriazoles (3Aa, 3Bb), where 2-azido-*N*-(4-chlorobenzylidene)aniline (4) led to 2-(4-chlorophenyl)benzimidazole (4a) in moderate yield (*ca.* 45%) together with *o*-azidoaniline

(4b) and *p*-chlorobenzaldehyde (4c). These latter products (4b) and (4c) arose from hydrolysis of unchanged azide (4) during aqueous work-up of the reaction mixture. Analogous results were obtained by using boron trifluoride instead of boron trichloride (Scheme 1). These findings suggest that azides–BX<sub>3</sub> complexes (I) or nitrenium–BX<sub>3</sub> complexes (II) resulting from (I) by loss of nitrogen are responsible for the formation of compounds (1a)–(4a) and (2b). These are formed by intramolecular 1,5- (and 1,6-) cyclisation of the complexes (I) or (II).

Thermolysis and photolysis of the azides (1) [to (1a)] and (2) [to (2a) and (2b)] are well known aryl nitrene reactions.<sup>8,9</sup> Thermal decomposition of the azides (3) and (4) is known to lead to the compounds (3a) and (4a) via an assisted intramolecular cyclisation process.<sup>10</sup> Cyclisation of 2-azidobiphenyl (1) to carbazole (1a) occurs effectively in the presence of AlCl<sub>3</sub>,<sup>5</sup> but not with TFA or TFSA.<sup>3</sup>

At room temperature in the presence of BF<sub>3</sub> or BCl<sub>3</sub> the *ortho*-nitro substituted azides (5) and (6) were found to be fairly stable presumably owing to their very weak basicity. However, these azides (5) and (6) underwent smooth decomposition at 50 °C in a few hours in the presence of either boron trichloride or trifluoride. The azide (5) gave 1-nitrocarbazole (5a) in fairly good yield (Scheme 1). No evidence of formation of 4-phenylbenzofuroxan (8) could be obtained. Pyrolysis of the azide (5) gave the benzofuroxan (8), but not the carbazole (5a).<sup>11</sup> As with the azide (5), *o*-nitrophenyl azide (6) gave no benzofuroxan (9).<sup>12</sup> The chlorinated nitroanilines (6a,b) were mainly formed, in addition to little amounts of *o*-nitroaniline (6c), on treatment of the azide (6) with boron trichloride. However, with boron trifluoride the azide (6) gave a high yield of *N*-*o*-nitrophenylaniline (6d) (Scheme 1). The chlorinated nitroanilines (6a,b) might result from an intermediate *o*-nitrophenylnitrenium–BCl<sub>3</sub> complex by transfer of chloride from boron to the activated 4- and 6-positions of the aryl nitrenium ring. On the other hand, the diarylamine (6d) might arise from electrophilic aromatic *N*-substitution of benzene by the corresponding nitrenium–BF<sub>3</sub> complex. The difference observed above is as a result of a lower migratory aptitude of fluoride with respect to chloride.

Our product and kinetic studies of the decomposition of phenyl azide (7) and 2-azidobiphenyl (1) in aromatic solvents in the presence of boron trifluoride–diethyl ether provided indirect evidence that aryl nitrenium–BX<sub>3</sub> complexes (II) are probably the reactive intermediates in the trihalogenoborane-

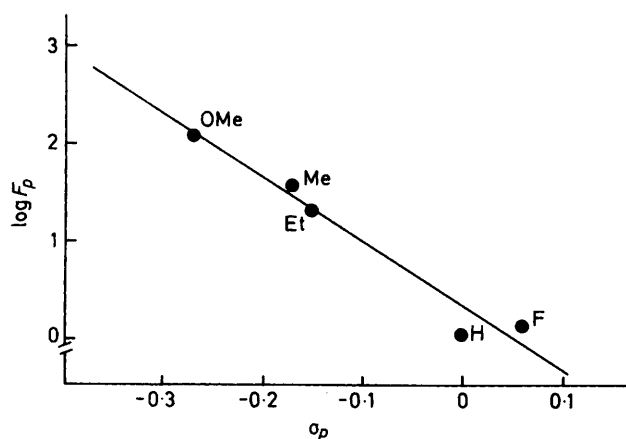


Scheme 1. Reagents: i,  $\text{BCl}_3$  or  $\text{BF}_3$ , benzene, 25 °C; ii,  $\text{BCl}_3$ , benzene, 50 °C; iii,  $\text{BF}_3$ , benzene, 50 °C

**Table 1.** Rate constants<sup>a</sup> and product yields<sup>b,c</sup> for decomposition of phenyl azide (7) in aromatic solvents in the presence of BF<sub>3</sub>-Et<sub>2</sub>O (1 mol equiv.)

| Solvent          | $K \times 10^5/s^{-1}$ | Products (%) |       |       |       |       |                    |      |       |       |
|------------------|------------------------|--------------|-------|-------|-------|-------|--------------------|------|-------|-------|
|                  |                        | (10)         | (11a) | (11b) | (12a) | (12b) | (13b) <sup>d</sup> | (14) | (15a) | (15b) |
| Benzene          | 1.6                    | 42           |       |       |       |       |                    |      |       |       |
| Toluene          | 1.2                    |              | 20    | 32    |       |       |                    |      |       |       |
| Ethylbenzene     |                        |              |       |       | 15    | 29    |                    |      |       |       |
| Fluorobenzene    |                        |              |       |       |       |       | 52                 |      |       |       |
| <i>m</i> -Xylene | 1.3                    |              |       |       |       |       |                    | 55   |       |       |
| Anisole          |                        |              |       |       |       |       |                    |      | 14    | 30    |

<sup>a</sup> For decomposition of phenyl azide (0.02M) at 75 °C. <sup>b</sup> Isolated yields based on starting phenyl azide (0.2M) referring to reactions carried out at 60 °C. <sup>c</sup> Little amounts of aniline were also generally observed. <sup>d</sup> Contaminated by the *ortho*-isomer (13a).



**Figure.** Plot of  $\log F_p$  against  $\sigma_p$  for the formation of diarylamines on treatment of phenyl azide with substituted benzenes at 60 °C in the presence of BF<sub>3</sub>-Et<sub>2</sub>O

promoted decomposition of the aryl azides (1)–(6) examined. The complete decomposition of phenyl azide (7) in benzene (0.2M) at 25 °C in the presence of boron trifluoride took place in a few min as indicated by t.l.c., but did not proceed essentially in the presence of boron trifluoride–diethyl ether even after 1 day. Evidently, the use of boron trifluoride complexed with diethyl ether instead of neat boron trifluoride largely disfavours the formation of the azide–BF<sub>3</sub> complex. However, in the presence of BF<sub>3</sub>-Et<sub>2</sub>O complete decomposition of the azide (7) could be achieved in *ca.* 12 h when the reaction temperature was raised to 60 °C. Column chromatography of the reaction mixture gave diphenylamine (10) (42%) in addition to small amounts of aniline and unidentifiable material. Under the same conditions, phenyl azide (7) in *m*-xylene afforded the diarylamine (14) (55%), whereas in anisole, toluene, ethylbenzene, and fluorobenzene mixtures of 2- and 4-substituted diphenylamines (11a)–(13a) and (15a)–(13b) and (15b) were obtained in moderate overall yields (Table 1).

The relative rate constants,  $F_p$ , for the formation of the *para*-substituted diphenylamines (11b)–(13b) and (15b) with respect to diphenylamine (10) were determined by treating the azide (7) (0.02M) with BF<sub>3</sub>-Et<sub>2</sub>O in suitable mixtures of benzene and appropriate mono-substituted benzene. A 0.02M solution of azide (7) was used here as we observed (g.l.c.) that yields of the resulting substitution products (11)–(13) and (15) were generally fairly high at this azide concentration, thus allowing confident determinations of relative rates. The correlation between  $\log F_p$  and  $\sigma_p$  gave a linear plot with  $\rho = -6.69$  (Figure). A similar  $\rho$ -value ( $-6.0$ ) has been previously observed for related aromatic substitutions of substituted benzenes by

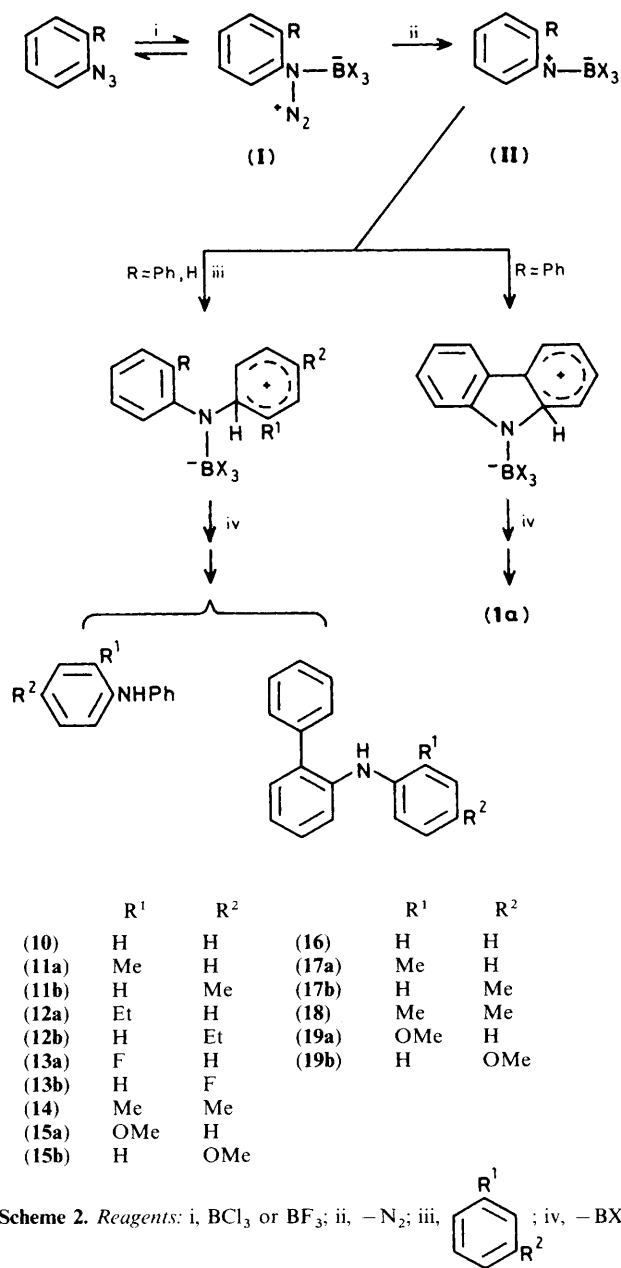
phenylnitrenium–AlCl<sub>3</sub> complex, resulting from the treatment of the azide (7) with aluminium chloride at room temperature.<sup>5</sup> Moreover, the pseudo-first-order rate constant ( $k_{\text{obs}}$ ) for the decomposition of this azide (7) at 75 °C in the presence of BF<sub>3</sub>-Et<sub>2</sub>O was found to be slightly greater in benzene than in toluene or *m*-xylene (Table 1).

These observations indicated that the phenyl azide–BF<sub>3</sub> complex (I) loses molecular nitrogen in a rate-determining step to give a nitrenium–BF<sub>3</sub> complex (II). This then effects electrophilic aromatic *N*-substitution of the solvent–substrate to give the diarylamines (10)–(15) (Scheme 2). The possibility that these compounds (10)–(15) might result from an S<sub>N</sub>2 mechanism involving nucleophilic attack by aromatic compounds on the phenyl azide–BF<sub>3</sub> complex (I) appears to be ruled out by the findings that the rate constant for the decomposition of the azide (7) is slightly greater in benzene than in toluene and *m*-xylene, which is contrary to what would be expected for an S<sub>N</sub>2 process. (The slight decrease in rate using the methylated benzene might be as a result of a more favourable charge-transfer interaction of boron trifluoride with these substrates than with benzene.)

The rate constant for the decomposition of 2-azidobiphenyl (1) at 75 °C in benzene in the presence of boron trifluoride–diethyl ether was found to be *ca.* five times as high as that of phenyl azide (7) (Table 2). As observed with phenyl azide (7), its value was found to be greater in benzene than in toluene or *m*-xylene (Table 2). Moreover, in these solvents and anisole at 60 °C, the azide (1) led to carbazole (1a) and the appropriate diarylamines [(16), (17a,b), (18), and (19a,b)], the formation of which depends greatly upon the nucleophilic character of the aromatic solvent (Table 2).

These results suggest that the nitrenium–BF<sub>3</sub> complex is also an intermediate in the decomposition of 2-azidobiphenyl (1). Thus, carbazole (1a) results from an intramolecular aromatic *N*-substitution of an intermediate biphenyl-2-yl nitrenium–BF<sub>3</sub> complex (II) (Scheme 2).

On the basis of these results, it may be confidently assumed that the decomposition of the azidobiphenyls (1), (2), and (5) at room temperature in the presence of boron chloride or fluoride proceeds *via* an analogous mechanism involving the nitrenium–trihalogenoborane complexes as intermediates. Arylnitrenium–BF<sub>3</sub> complexes are also conceivable intermediates in the BX<sub>3</sub>-promoted decomposition of the aryl azides (3A,B) and (4), but in such cases we cannot exclude possible assistance by the *ortho*-substituent in the elimination of nitrogen from the first formed azide–BX<sub>3</sub> complexes. Thus, our present results show that the treatment of boron chloride or fluoride with aryl azides bearing an *ortho*-aryl-, diazoaryl, or -aryloxy substituent can smoothly lead to fused azoles by intramolecular 1,5-cyclisation with aryl nitrenium–trihalogenoborane complexes as intermediates. These reactions offer a new facile route to fused azoles.



Moreover, in the light of our present and previous findings<sup>6,7,13</sup> it may be inferred that singlet arylnitrenium-trihalogenoborane complexes, irrespective of the substituent present in the phenyl ring, preferentially bear the positive charge on the nitrogen atom rather than on the *ortho*- and *para*-positions. In fact, we have found general evidence for intra- or inter-molecular *N*-attack of nitrenium-BX<sub>3</sub> complexes, exclusive of *C*-attack.

The chemical trend exhibited by these complexes resembles that of arylnitrenium-AlCl<sub>3</sub> complexes,<sup>5</sup> but it not consistent with that shown by arylnitrenium ions, whose selectivity for *N*- or *C*-attack depends upon the electronic character of substituents.<sup>3</sup> The regioselective *N*-attack of arylnitrenium-AlCl<sub>3</sub> complexes has been ascribed to the greater delocalization of the positive charge between the nitrogen and aluminum atoms than is possible on the phenyl ring. We suggest that in the arylnitrenium-trihalogenoborane complexes, delocalisation of the positive charge over the phenyl ring would be disfavoured

**Table 2.** Rate constants<sup>a</sup> and product yields<sup>b,c</sup> for decomposition of 2-azidobiphenyl (1) in aromatic solvents in the presence of BF<sub>3</sub>-Et<sub>2</sub>O (1 mol equiv.)

| Solvent          | K × 10 <sup>5</sup> s <sup>-1</sup> | Products (%) |      |       |       |      |       |       |
|------------------|-------------------------------------|--------------|------|-------|-------|------|-------|-------|
|                  |                                     | (1a)         | (16) | (17a) | (17b) | (18) | (19a) | (19b) |
| Benzene          | 8.2                                 | 92           | 3    |       |       |      |       |       |
| Toluene          | 4.5                                 | 52           |      | 8     | 35    |      |       |       |
| <i>m</i> -Xylene | 5.3                                 | 46           |      |       |       | 46   |       |       |
| Anisole          |                                     | 3            |      |       |       |      | 11    | 85    |

<sup>a</sup> For decomposition of the azide (1) (0.02M) at 75 °C. <sup>b</sup> Isolated yields based on starting azide (0.2M) for reactions run at 60 °C. <sup>c</sup> Trace amounts of 2-aminobiphenyl were also generally produced.

owing to the unfavourable effect of increasing the separation of the opposite charges located on the adjacent nitrogen and boron atoms.

### Experimental

Commercial BCl<sub>3</sub> and BF<sub>3</sub> were purchased from Matheson. Carbazole (1a), 2-nitroaniline (6c), diphenylamine (10), 4-chlorobenzaldehyde (4c), and BF<sub>3</sub>-Et<sub>2</sub>O were RPE Farmitalia C. Erba reagents. The known starting azides (1)–(7) were all prepared from the corresponding amines by diazotization followed by treatment with sodium azide.<sup>14</sup> Solvents were purified and dried by standard methods.<sup>15</sup>

I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrometer. <sup>1</sup>H N.m.r. spectra were recorded on a Varian EM 360 L 60 MHz instrument for solutions in CDCl<sub>3</sub> using TMS as internal standard. Mass spectra were recorded on a JEOL DMS 100 instrument. Analytical g.l.c. was performed on a Varian 3700 chromatograph using a H.P. column filled with 5% OV 101 CHROM.G.H.P. 100/120, 50 cm × 1/8".

*Reaction of Azido Derivatives (1)–(6) with Boron Trichloride or Trifluoride in Benzene. General Procedure.*—A solution of azide (1)–(6) (2.5 mmol) in benzene (5 ml) was slowly added to a stirred solution of BCl<sub>3</sub> or BF<sub>3</sub> (ca. 2.6 mmol) in benzene (15 ml) and the mixture allowed to stand at room temperature for 10 min, after which t.l.c. showed that no starting material remained. The mixture was evaporated, the residue carefully treated with aqueous sodium carbonate, and extracted twice with CH<sub>2</sub>Cl<sub>2</sub>. The extracts were combined and the resulting organic layer was washed with water, dried, and evaporated. The residue was chromatographed on a silica gel column using hexane containing a gradually increasing amount of diethyl ether as eluant.

*Reaction of 2-azidobiphenyl (1).* Chromatography gave pure carbazole (1a) [0.39 g, 92% (BCl<sub>3</sub>) and 0.40 g, 94% from (BF<sub>3</sub>)], m.p. and mixed m.p. 245–246 °C.

*Reaction of 2-azido-2'-phenylazobiphenyl (2).* With BCl<sub>3</sub> this reaction afforded (i) benzo[*c*]cinnoline *N*-phenylimide (2b) (0.43 g, 63%), m.p. 130–131 °C (lit.<sup>9</sup> 129–131 °C); (ii) 2-amino-2'-phenylazobiphenyl (2c) (2%), identical in all respects with an authentic sample;<sup>9</sup> (iii) 4-phenylazocarbazole (2a) (0.14 g, 20%), m.p. 190–191 °C (lit.<sup>9</sup> 190–191 °C).

The yields were found to be substantially unchanged using BF<sub>3</sub>.

*Reaction of 2-azido-4'-chloroazobenzene (3A).* Chromatography gave 2-(4-chlorophenyl)benzotriazole (3Aa) [0.51 g, 90% (BCl<sub>3</sub>) and 0.54 g, 94% (BF<sub>3</sub>)], m.p. 168–170 °C (lit.<sup>16</sup> 167.5–168.5 °C); *m/z* 229 (*M*<sup>+</sup>, 100), 125 (70), 111 (10), and 90 (50).



*Reaction of 2-azidoazobenzene (3B).* Chromatography afforded 2-phenylbenzotriazole (**3Ba**) [0.46 g, 94% ( $\text{BCl}_3$ ) and 0.45 g, 92% ( $\text{BF}_3$ )], m.p. and mixed m.p. 108–109 °C (lit.,<sup>16</sup> 109 °C).

*Reaction of 2-azido-N-(4-chlorobenzylidene)aniline (4).* Chromatography gave (i) 4-chlorobenzaldehyde (**4c**) (48–50%), m.p. and mixed m.p. 47 °C; (ii) 2-azidoaniline (**4b**) (40–44%), m.p. 60–61 °C (lit.,<sup>17</sup> m.p. 60–61 °C);  $\nu_{\text{max.}}$  (KBr) 3 520 and 3 420 ( $\text{NH}_2$ ), and 2 130  $\text{cm}^{-1}$  ( $\text{N}_3$ ); (iii) 2-(4-chlorophenyl)-benzimidazole (**4a**) [0.24 g, 41% ( $\text{BCl}_3$ ) and 0.26 g, 44% ( $\text{BF}_3$ )], m.p. 293–295 °C (lit.,<sup>17</sup> m.p. 296 °C);  $m/z$  228 ( $M^+$ ) and 194;  $\delta_{\text{H}}$  (60 MHz,  $\text{CDCl}_3$ ) 7.7 (4 H, q,  $J$  5.1 Hz) and 7.3 (4 H, q,  $J$  5.2 Hz).

*Reaction of 2-azido-3-nitrobiphenyl (5).* The general procedure was followed except that the reaction mixture was heated at 50 °C for 6 h. Chromatography gave 1-nitrocarbazole (**5a**) [0.45 g, 70% ( $\text{BCl}_3$ ) and 0.48 g, 75% ( $\text{BF}_3$ )], m.p. 186–188 °C (lit.,<sup>18</sup> m.p. 186–187 °C);  $\nu_{\text{max.}}$  (KBr) 3 400  $\text{cm}^{-1}$  (NH);  $m/z$  212 ( $M^+$ , 100%) and 166 ( $M^+ - 46$ , 55); in addition to trace amounts of 2-amino-3-nitrobiphenyl<sup>11</sup> and tarry material.

*Reaction of 2-nitrophenyl azide (6).* (a) With  $\text{BCl}_3$ . This reaction was carried out at 50 °C for ca. 6 h. The following products were obtained in order of elution: (i) 2-chloro-6-nitroaniline (**6b**) as a yellow–orange solid (0.07 g, 17%), m.p. 75–76 °C (lit.,<sup>19</sup> 76 °C); (ii) 2-nitroaniline (**6c**) (0.01 g, 3%), m.p. and mixed m.p. 71–72 °C; (iii) 4-chloro-2-nitroaniline (**6a**) (0.28 g, 64%), identical in all respects with a commercial sample.

(b) With  $\text{BF}_3$ . This reaction was similarly carried out at 50 °C for ca. 6 h. Chromatography gave *N*-*o*-nitrophenylaniline (**6d**) (0.44 g, 82%), m.p. 76–77 °C (lit.,<sup>20</sup> 76 °C);  $\nu_{\text{max.}}$  (KBr) 3 360 (NH) and 1 360  $\text{cm}^{-1}$  ( $\text{NO}_2$ );  $m/z$  214 ( $M^+$ , 100), 197 ( $M^+ - 17$ , 16), 178 (22), and 167 (66).

*Reaction of 2-Azidobiphenyl (1) in Aromatic Solvents in the Presence of  $\text{BF}_3\text{-Et}_2\text{O}$ .*—The azide (**1**) (4.0 mmol) in benzene, toluene, anisole, or *m*-xylene (20 ml) was treated with  $\text{BF}_3\text{-Et}_2\text{O}$  (4.0 mmol) at 60 °C, for 6–8 h. After evaporation of the solvent, the residue was treated with aqueous sodium carbonate, and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was dried and the solvent evaporated. Carbazole (**1a**) and the diarylamines [(**16**),<sup>21</sup> (**17a,b**), (**18**), and (**19a,b**)] were isolated by column chromatography on silica gel by gradual elution with hexane and hexane–diethyl ether. Yields, as determined by g.l.c. using 4-aminobiphenyl as the marker, are reported in Table 2. The following new compounds were thus obtained:

2-*o*-Toluidinobiphenyl (**17a**), as an oil,  $\nu_{\text{max.}}$  3 420 (NH), 760, and 720  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (60 MHz,  $\text{CDCl}_3$ ) 7.35 (5 H, br s), 7.12 (8 H, m), 5.43 (1 H, s), and 2.04 (3 H, s);  $m/z$  259 ( $M^+$ , 100), 243 (5), and 180 (5) (Found: C, 88.05; H, 6.65; N, 5.35.  $\text{C}_{19}\text{H}_{17}\text{N}$  requires C, 88.0; H, 6.6; N, 5.4%).

2-*p*-Toluidinobiphenyl (**17b**), m.p. 54–55 °C;  $\nu_{\text{max.}}$  3 420 (NH), 820, 760, and 710  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (60 MHz,  $\text{CDCl}_3$ ) 7.35 (5 H, br s), 7.13 (8 H, m), 5.50 (1 H, br s), and 2.32 (3 H, s);  $m/z$  259 ( $M^+$ , 100) and 243 ( $M^+ - 16$ , 10) (Found: C, 88.1; H, 6.55; N, 5.4%).

2-(2,4-Xylydino)biphenyl (**18**), as an oil,  $\nu_{\text{max.}}$  (liq. film) 3 430 (NH), 780, 760, and 715  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (60 MHz,  $\text{CDCl}_3$ ) 7.40 (5 H, br s), 7.00 (7 H, m), 5.31 (1 H, s), 2.34 (3 H, s), and 2.00 (3 H, s);  $m/z$  273 ( $M^+$ , 100), 258, 257, 256, and 243 (Found: C, 87.7; H, 6.95; N, 5.15.  $\text{C}_{20}\text{H}_{19}\text{N}$  requires C, 87.85; H, 7.0; N, 5.1%).

2-*o*-Anisidinobiphenyl (**19a**), as an oil,  $\nu_{\text{max.}}$  3 400 (NH), 750, and 715  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  (60 MHz,  $\text{CDCl}_3$ ) 7.70 (5 H, br s), 7.15 (8 H, m), 6.22 (1 H, s), and 3.80 (3 H, s);  $m/z$  275 ( $M^+$ , 100), 260 ( $M^+ - 15$ , 46), and 166 (21) (Found: C, 83.0; H, 6.15; N, 5.15.  $\text{C}_{19}\text{H}_{17}\text{NO}$  requires C, 82.9; H, 6.2; N, 5.1%).

2-*p*-Anisidinobiphenyl (**19b**), m.p. 43–44 °C;  $\nu_{\text{max.}}$  3 410 (NH), 830, 780, 760, and 715  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  7.52 (5 H, br s), 7.02 (8 H,

br q), and 3.74 (3 H, br);  $m/z$  275 ( $M^+$ , 100), 260 ( $M^+ - 15$ , 63), and 166 (24) (Found: C, 82.85; H, 6.15; N, 5.05%).

*Rates of Decomposition of 2-Azidobiphenyl (1) and Phenyl Azide (7).*—A mixture of the azide (**1**) or (**7**) (0.2 mmol) and  $\text{BF}_3\text{-Et}_2\text{O}$  (0.2 mmol) in benzene, toluene, or *m*-xylene (10 ml) was allowed to react in a thermostatic bath at 75 °C. The rates of decomposition of the azides (**1**) and (**7**) were determined by i.r. spectroscopic measurement of the neat  $\text{N}_3$  band (ca. 2 100  $\text{cm}^{-1}$ ) as a function of time. The results are summarized in Tables 1 and 2.

*Hammett Plot Determination for Phenyl Azide (7).*—A solution of phenyl azide (**7**) (0.2 mmol) and  $\text{BF}_3\text{-Et}_2\text{O}$  (0.2 mmol), in a mixture of benzene and toluene (20:1), benzene and anisole (30:1), benzene and ethylbenzene (10:1), or benzene and fluorobenzene (1:1) (10 ml) was allowed to react in a thermostatic bath at 60 °C. After ca. 8 h the reaction mixtures were treated as previously described and then the relative yields of (**10**) to (**11b**), (**12b**), (**13b**), and (**15b**), respectively were determined by quantitative g.l.c.

The analyses agreed within <5% in three runs. The partial *para*-attacking rate factors ( $F_p$ ) for toluene, anisole, ethylbenzene, and fluorobenzene were calculated on the basis of the above product ratios, which have been suitably corrected for the different molar ratios of the aromatic solvents used. The correlation between  $\log F_p$  and  $\sigma_p$  gave a linear plot with  $\rho = -6.69$  (0.957 coefficient of correlation).

*Reaction of Phenyl Azide (7) with  $\text{BF}_3\text{-Et}_2\text{O}$  in Aromatic Solvents.*—A solution of phenyl azide (**7**) (4.0 mmol) and  $\text{BF}_3\text{-Et}_2\text{O}$  (4.0 mmol) in benzene, toluene, ethylbenzene, fluorobenzene, *m*-xylene, or anisole (20 ml) was heated at 60 °C until t.l.c. showed no starting material remained (8–10 h). The excess of solvent was distilled off at 15 mmHg; the residue was treated with aqueous sodium carbonate and then extracted twice with  $\text{CH}_2\text{Cl}_2$ . Column chromatography on silica gel gave the diarylamines (**10**), (**11a,b**),<sup>22</sup> (**12a,b**),<sup>23</sup> (**13b**),<sup>24</sup> (**14**), and (**15a,b**).<sup>25</sup> The yields are shown in Table 1. Trace amounts of aniline and tarry material were also generally isolated.

The previously unknown *N*-phenyl-2,4-xylydene (**14**) was obtained as an oil,  $\nu_{\text{max.}}$  3 400  $\text{cm}^{-1}$  (NH);  $\delta_{\text{H}}$  (60 MHz,  $\text{CDCl}_3$ ) 7.00 (8 H, m), 5.27 (1 H, s), 2.33 (3 H, s), and 2.23 (3 H, s);  $m/z$  197 ( $M^+$ , 100), 182 (12), 181 (11), and 180 (12) (Found: C, 85.2; H, 7.55; N, 7.05.  $\text{C}_{14}\text{H}_{15}\text{N}$  requires C, 85.3; H, 7.6; N, 7.1%).

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