# Intramolecular Addition of Aryl Radicals to the Azo-group. Part 2.[1] Production of Some *N*-(Carbazol-9-yl)arylaminyl Radicals and Their Reactivity

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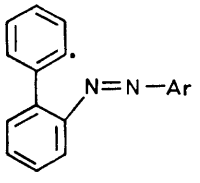
The *N*-(carbazol-9-yl)arylaminyl radicals (2a—d) have been produced by intramolecular addition of the 2'-arylazobiphenyl-2-yl radicals (1a—d) generated by reduction of the corresponding arenediazonium tetrafluoroborates (3a—d) and their reactivity has been investigated. *N*-(Carbazol-9-yl)-4-tolylaminyl (2a) and *N*-(carbazol-9-yl)-4-chlorophenylaminyl (2b) exhibit N,N-coupling at −20° C, whereas hydrogen abstraction and $C_{ortho}$,N-coupling appear to be the main reaction paths at room temperature. A comparable trend has been observed with 1-(4-chlorophenyl)-2,2-diphenylhydrazyl radicals (14) generated by oxidation of the corresponding hydrazine (13) with lead dioxide. From the *N*-(carbazol-9-yl)biphenyl-2-ylaminyl radicals (2c) and (2d) some evidence has been obtained that they are capable of undergoing intramolecular addition to aromatic rings.

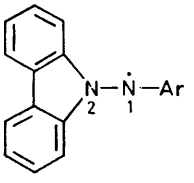
We reported previously[1] that 2'-phenylazobiphenyl-2-yl radicals (1; Ar = Ph) undergo intramolecular 1,5-addition to the azo-group to give *N*-(carbazol-9-yl)-phenylaminyl radicals (2; Ar = Ph), from which the hydrazine (5; R = H) is formed at low temperature by N,N-coupling; the hydrazine (5; R = H) is thermally unstable and easily fragments at room temperature to give back the hydrazyl radicals (2; Ar = Ph). On this basis intramolecular addition of the 2'-arylazobiphenyl-2-yl radicals (1) offers a convenient route to the *N*-(carbazol-9-yl)arylaminyl radicals (2), suitable for a study of their chemistry.

Results obtained from the *N*-(carbazol-9-yl)phenylaminyls (2; Ar = Ph) indicate that they are reactive species which, at room temperature, furnish hydrogen abstraction products, *i.e.*, *N*-carbazol-9-ylaniline (6; R = H), and a compound which was assigned structure (4), apparently deriving from preliminary $C_{para}$,N-coupling and subsequent isomerization.



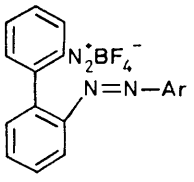
(1)

a; Ar = 4-$MeC_6H_4$
b; Ar = 4-$ClC_6H_4$



(2)

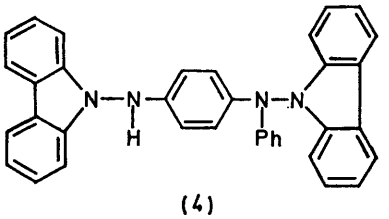
c; Ar = 2-$PhC_6H_4$
d; Ar = 2-(3,5-$Me_2C_6H_3$)$C_6H_4$



(3)

We now report results of a study of the chemical behaviour of the *N*-(carbazol-9-yl)arylaminyl radicals (2a—d). All these radicals (2) were generated from the aryl radicals (1) which were in turn produced by reduction of the corresponding 2'-arylazobiphenyl-2-diazonium tetrafluoroborates (3a—d) with sodium iodide.[1]

Addition of sodium iodide to a solution in acetone of the tetrafluoroborate (3a) at −20 °C led to the formation of the hydrazine (5a) in 84% yield, a result analogous to that observed in the reduction of 2'-phenylazobiphenyl-2-diazonium tetrafluoroborate (3; Ar = Ph). The hydrazine (5a) readily undergoes fragmentation in benzene solution at room temperature to give the *o*-phenylenediamine (7a) (75%), *N*-carbazol-9-yl-4-toluidine (6a) (10%), carbazole (8) (3%), and trace amounts of 2,7-dimethylphenazine (9a) and 4,4'-dimethylazobenzene (10a) (Scheme 1).



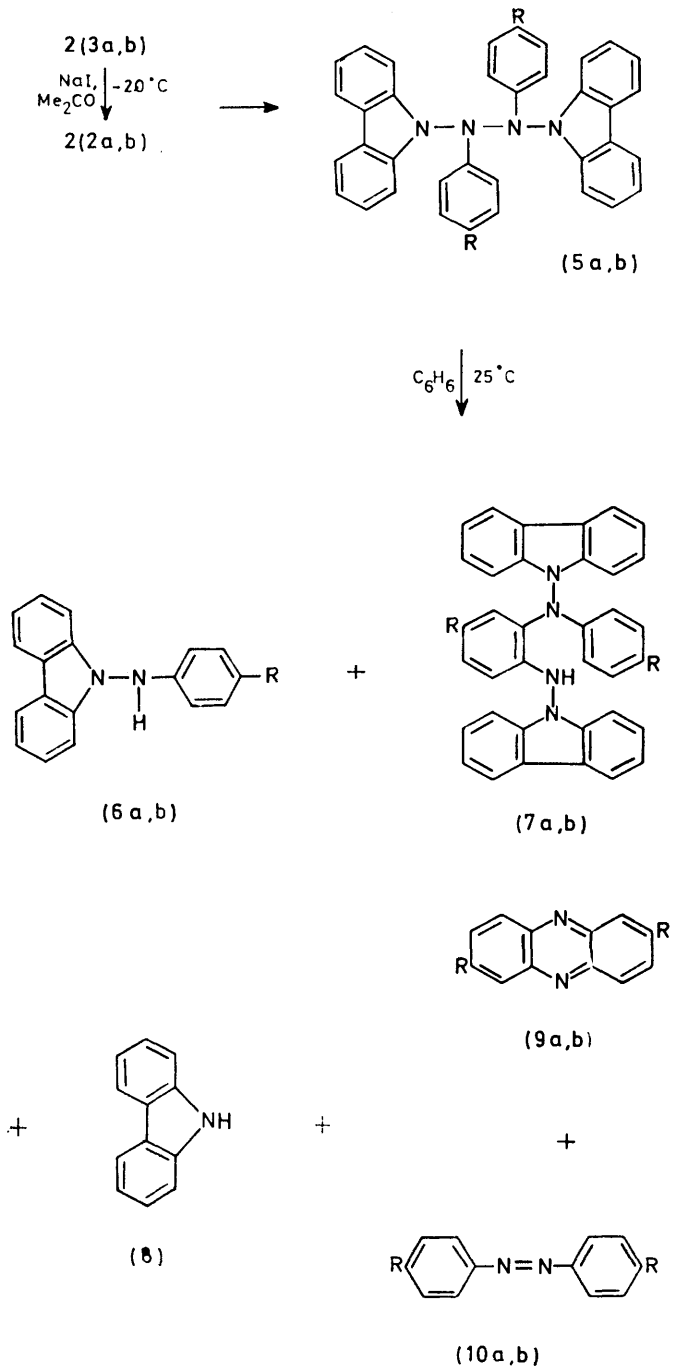
(4)

The structure of compound (7a) was assigned on the basis of elemental analysis and spectral and chemical evidence. The i.r. spectrum showed N–H stretching absorption at 3 340 $cm^{-1}$; the n.m.r. spectrum showed two methyl peaks at δ 2.1 and 2.31 and a complex pattern due to 23 protons in the aromatic region. The mass spectrum did not show the parent ion but prominent fragment ions were present at *m/e* 374, 208, 167, 166, 140, and 139. The ion at *m/e* 374 arising from loss of $C_{12}H_{10}N$ from the molecular ion can reasonably be attributed to the 2,7-dimethyl-5-(carbazol-9-yl)phenazinium ion ($C_{26}H_{20}N_3^+$); the ion at *m/e* 208 formed by loss of a carbazolyl radical from $C_{26}H_{20}N_3^+$ might be due to the 2,7-dimethylphenazine ion ($C_{14}H_{12}N_2^+$); finally ions at *m/e* 167 and 166 can be assigned to the carbazole and carbazolyl species, $C_{12}H_9N^+$ and $C_{12}H_8N^+$, respectively, from which ions at *m/e* 140 and 139 are formed by loss of HCN.

Thermal decomposition of compound (7a) in refluxing degassed benzene furnished carbazole (8) (2 mol. equiv.) and 2,7-dimethylphenazine (9a) (1 mol. equiv.) in almost quantitative yield. Qualitative experiments showed that u.v. irradiation of compound (7a) in benzene solution and oxidation with lead dioxide or silver oxide led to substantially the same results. However formation of carbazole (8) and the phenazine (9a) appeared to be less clean in these latter cases, being accompanied by some coloured products.

Under all conditions investigated we had no evidence

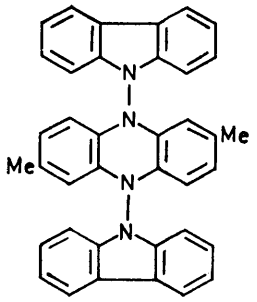
for formation of the dihydrophenazine (11a), which could conceivably arise from intramolecular cyclization of the *o*-phenylenediamine (7a) by analogy with the mechanism postulated for the formation of 5,10-diaryl-




SCHEME 1 a; R = Me. b; R = Cl

5,10-dihydrophenazines from *para*-substituted diarylaminyl radicals.[2]

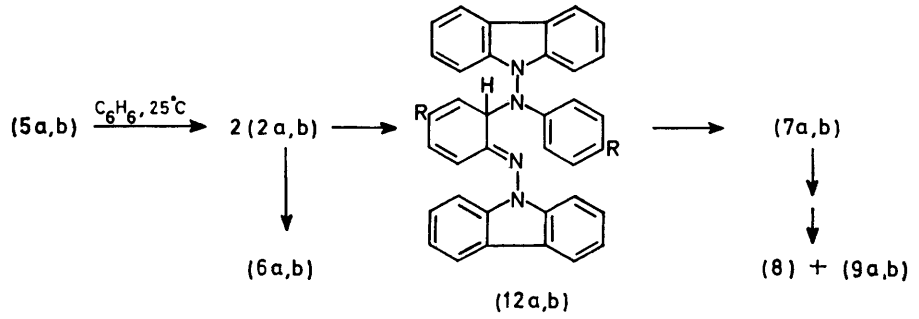
Similar results were obtained from reduction of the 4-chlorophenyl compound (3b) at −20 °C. The corresponding N,N-coupling product (5b) was isolated in 90% yield. Fragmentation of (5b) at room temperature furnished the *o*-phenylenediamine (7b) (60%), *N*-carbazol-9-yl-4-chloroaniline (6b) (15%), carbazole (8) (10%), 2,7-dichlorophenazine (9b) (3%), and 4,4'-dichloroazobenzene (10b) (Scheme 1). Formation of compounds (7a, b) from thermal fragmentation of the N,N-dimers (5a, b) can be most reasonably explained by preliminary $C_{ortho}$,N-coupling of the carbazoylhydrazyls (2a, b) leading to (12a, b), followed by isomerization to (7a, b); on the other hand formation of the N-carbazol-9-ylanilines (6a, b) can be attributed to hydrogen abstraction by the radicals (2a, b), whereas carbazole (8) and the phenazines (9a, b) most likely derive from decomposition of the *o*-phenylenediamines (7a, b) (Scheme 2).




From our findings obtained with the *N*-(carbazol-9-yl)arylaminyls (2a, b) together with related results [1] from the *N*-(carbazol-9-yl)phenylaminyl radicals (2; Ar = Ph) it may be inferred that all these carbazolylhydrazyls (2) readily undergo N,N-dimerization at low temperature, whereas at room temperature hydrogen abstraction and C,N-dimerization appear to be the predominant reaction paths. Moreover it seems that $C_{para}$, N-coupling is preferred over $C_{ortho}$,N-coupling, unless substituents are present in the *para*-position of the phenyl ring of the hydrazyls (2), in which case $C_{ortho}$,N-coupling occurs almost exclusively.

Since triarylhydrazyl radicals so far have been investigated mainly by e.s.r. spectroscopy,[2b,3] whereas their organic chemistry is yet almost unexplored,[2b,3] we turned our attention to a study of the 1-(4-chlorophenyl)-2,2-diphenylhydrazyl radical (14) in order to ascertain whether a triarylhydrazyl, carrying a substituent in the *para*-position of the aryl ring on N(1), might show chemical behaviour analogous to that exhibited by the carbazoylhydrazyls (2a, b), thus pointing to a general trend, irrespective of the nature of the aromatic system on N(2).

Goldschmidt and his co-workers [4] have reported the preparation of 1-(4-chlorophenyl)-2,2-diphenylhydrazyl (14) by oxidation of the corresponding hydrazine (13) and the original observation that the radical (14) appeared to be longer-lived than triphenylhydrazyl was taken as evidence that the presence of the chloro-substituent in the *para*-position enhances the stability



SCHEME 2 a; R = Me: b; R = Cl

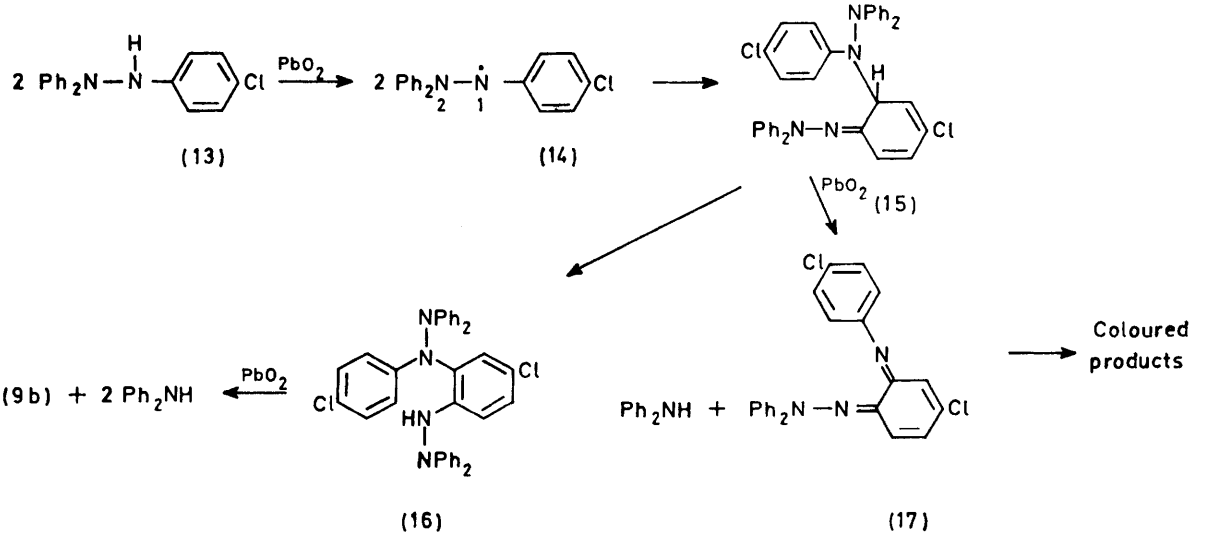
of triphenylhydrazyls by preventing their decomposition through $C_{para}$,N-coupling.[3] However no mention of any products deriving from decomposition of the radicals (14) was made in that report.[4]

Treatment of a solution in ether of 2-(4-chlorophenyl)-1,1-diphenylhydrazine (13) with lead dioxide at room temperature afforded diphenylamine (77%), tetraphenylhydrazine (9%), 2,7-dichlorophenazine (9b) (21%), and 4,4′-dichloroazobenzene (10b) (6%), as well as intractable coloured products.

Formation of the products diphenylamine, tetraphenylhydrazine, and particularly of 2,7-dichlorophenazine (9b) could be rationalized by assuming $C_{ortho}$,N-coupling of the radicals (14) to give (15); following isomerization to (16), (15) would be expected to be rapidly converted by lead dioxide into the phenazine (9b) and diphenylamine by analogy with the behaviour of the phenylenediamines (7a, b), whose decomposition was shown to occur fairly rapidly in the presence of lead dioxide at room temperature to afford carbazole (8) and the phenazines (9a, b) as major products. However the rather low yield of phenazine (9b) and formation of diphenylamine (and tetraphenylhydrazine) in high yield as well as considerable amounts of coloured products are indicative that in the presence of lead dioxide there might be a competitive fragmentation path available to the $C_{ortho}$,N-coupling product (15). A tentative explanation is that lead dioxide brings about some oxidation of the dimer (15) before its isomerization to compound (16), affording diphenylamine [and then tetraphenylhydrazine and the *o*-quinone di-imine (17)], from which coloured products are eventually formed (Scheme 3).

The same trend was observed in qualitative experiments with *N*-(carbazol-9-yl)-4-toluidine (6a) and 4-chloro-*N*-carbazol-9-ylaniline (6b), oxidation of which with lead dioxide under the same conditions as used in the case of the hydrazine (13) produced considerable amounts of coloured products as well as carbazole (8) and the phenazines (9a, b). As expected the *o*-phenylenediamines (7a, b) were also absent in these cases.

Formation of trace amounts of 4,4′-dichloroazobenzene (10b) and 4,4′-dimethylazobenzene (10a) from decomposition of the N,N-dimers (5a, b) and formation of (10b) to a somewhat greater degree from oxidation of the hydrazine (13) deserves comment, particularly since we did not observe formation of azobenzene from decomposition of the hydrazine (5; R = H)[1] and azobenzene could not be detected in the oxidation of triphenylhydrazine with lead dioxide.[5] Thus it seems that formation of azobenzenes occurs only when the phenyl group on N(1) of the hydrazyl radicals is *para*-substituted. All our findings, together with related reports

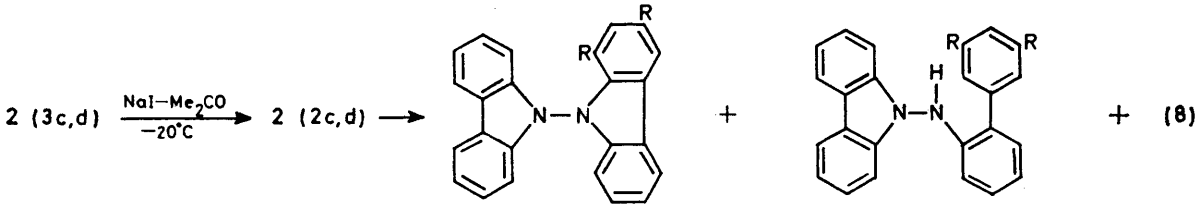


SCHEME 3

on triarylhydrazyls [3] and *N*-(carbazol-9-yl)phenylaminyls,[1] lead to the conclusion that the chemical behaviour of all these hydrazyls is substantially independent of the nature of the aromatic system on N(2). Moreover their behaviour shows a strong analogy with that of arylaminyl radicals; [2] they can be considered as a special type of arylaminyl radical.

Finally we prepared and investigated the reactivity of the *N*-(carbazol-9-yl)biphenyl-2-ylaminyl radicals (2c, d) in the hope of determining whether or not hydrazyl radicals are capable of adding to aromatic rings, at least intramolecularly. In fact, if intramolecular addition of the radicals (2c, d) to the *ortho'*-position of the biphenyl ring should occur, stable and isolable products, *i.e.* the bicarbazol-9-yls (18a, b), would be expected to be formed and thus their possible formation could provide diagnostic evidence for the intramolecular addition.

Reduction under normal conditions of the tetrafluoroborates (3c, d) at −20 °C did not lead to products derived from N,N-dimerization of the hydrazyls (2c, d), most probably owing to steric shielding of the aminyl nitrogen,




SCHEME 4 a; R = H: b; R = Me

and the bicarbazol-9-yls (18a, b) (5—6%), 2-(*N*-carbazol-9-ylamino)biphenyls (19a, b) (34—37%), and carbazole (8) (5—8%) were the only identifiable products after column chromatography of the reaction mixtures (Scheme 4).

Formation of the bicarbazol-9-yls (18a, b), although in very low yields, leads to the conclusion that, at least in these cases, carbazolylhydrazyls are indeed capable of undergoing intramolecular addition to aromatic rings. This view is further supported by our observations that conversion of the 2-(*N*-carbazol-9-ylamino)biphenyls (19a, b) into the bicarbazolyls (18a, b) can also be brought about by oxidation with lead dioxide or silver oxide at room temperature and on heating in benzene solution in the presence of an excess of chloranil.

Although the mechanism of these cyclizations requires further investigation, it seems that intramolecular addition to aromatic rings should be considered as another reaction path which the carbazolylhydrazyls (2) are capable of undergoing in addition to those examined above.

## EXPERIMENTAL

I.r. data are for carbon disulphide solutions, and u.v. data for solutions in 95% ethanol. Mass spectra were recorded with a JEOL JHS-D100 spectrometer. Reaction products, carbazole, bicarbazol-9-yl,[6] 2,7-dimethylphenazine,[7] 2,7-dichlorophenazine,[8] 4,4'-dimethylazobenzene,[9] 4,4'-dichloroazobenzene,[10] tetraphenylhydrazine,[11] and diphenylamine were characterized by mixed m.p. determination and i.r. spectral comparison with authentic samples which were prepared according to literature methods or were commercially available. 2-Amino-2'-(4-tolylazo)biphenyl, 2-amino-2'-(4-chlorophenylazo)biphenyl, and 2-amino-2'-(biphenyl-2-ylazo)biphenyl were prepared as described in the literature.[12]

*3',5'-Dimethyl-2-nitrosobiphenyl.*—A solution of 2-amino-3',5'-dimethylbiphenyl [13] (10 g) in chloroform (70 ml) was added dropwise to a solution of *m*-chloroperoxybenzoic acid (18 g) in chloroform (600 ml) at 0 °C. The resulting mixture was stirred at 0 °C for 15 min, then refluxed for 10 min, and poured into an excess of water. The organic layer was separated off, washed several times with 10% aqueous sodium hydroxide, and dried. Evaporation left a residue which was chromatographed on silica gel. Elution with 2% ether–petroleum afforded *3',5'-dimethyl-2-nitrosobiphenyl* (4.6 g, 44%), m.p. 103—104 °C, *m/e* 211 ($M^+$) (Found: C, 79.45; H, 6.4; N, 6.7. $C_{14}H_{13}NO$ requires C, 79.6; H, 6.2; N, 6.6%).

*2-Amino-2'-(3',5'-dimethylbiphenyl-2-ylazo)biphenyl.*—3',5'-Dimethyl-2-nitrosobiphenyl (4.6 g) in dichloromethane (20 ml) was added over 20 min to a solution of 2,2'-diaminobiphenyl (3.5 g) in acetic acid–dichloromethane (1 : 1; 50 ml). The resulting mixture was refluxed on a steam-bath for 30 min, then poured into an excess of water, and basified with sodium carbonate. Extraction with ether and evaporation of the extracts gave an oily residue which was chromatographed on silica gel. Elution with 10% ether–petroleum furnished *2-amino-2'-(3',5'-dimethylbiphenyl-2-ylazo)biphenyl* [parent amine of the diazonium salt (3d)] (2 g, 35%) as a red, thick oil which did not solidify, $\nu_{max.}$ 3 470 and 3 380 $cm^{-1}$ ($NH_2$), *m/e* 377 ($M^+$), 362, 361, 209, 197, 181, 168, 167, 166, 140, and 139 (Found: C, 81.7; H, 6.0; N, 12.35. $C_{26}H_{23}N_3$ requires C, 81.7; H, 6.1; N, 12.2%).

*Preparation and Reduction of 2'-(Arylazo)biphenyl-2-diazonium Tetrafluoroborates* (3a—d).—*General procedure.* The appropriate 2-amino-2'-arylazobiphenyl (6.2 mmol) was suspended in hydrochloric acid (3 ml) and water (20 ml) and diazotized at 0 °C with a solution of sodium nitrite (0.5 g) in water (10 ml). The mixture was stirred at 0 °C for 1 h, and then a solution of sodium tetrafluoroborate (1 g) in water (10 ml) was added dropwise to the stirred solution. The precipitated tetrafluoroborates (3a—d) were washed with a little cold water and dried overnight. The salts so obtained (4.8 mmol) were then suspended in dry acetone (20 ml) and treated at −20 °C with a solution of sodium iodide (1.1 g) in acetone (10 ml). The mixtures were stirred for 1 h at −20 °C and products were isolated either

by filtration or removal of the excess of the solvent by distillation and chromatography of the resulting residue.

Reduction of 2′-(4-tolylazo)biphenyl-2-diazonium tetrafluoroborate (3a) after filtration of the reaction mixture gave 1,2-*dicarbazol*-9-*yl*-1,2-*di*-(4-*tolyl*)*hydrazine* (5a) (84%) as white plates, m.p. 121—123 °C (decomp.), *m/e* 542 ($M^+$), 272, 208, 167, 166, 140, and 139 (Found: C, 83.2; H, 5.5; N, 10.4. $C_{38}H_{30}N_4$ requires C, 84.1; H, 5.6; N, 10.3%). Similarly, the 4-chlorophenylazo-compound (3b) furnished 1,2-*dicarbazol*-9-*yl*-1,2-*bis*-(4-*chlorophenyl*)*hydrazine* (5b) (90%) as white plates, m.p. 130—131 °C (decomp.), *m/e* 582 ($M^+$), 292, 248, 167, 166, 140, and 139 (Found: C, 74.45; H, 4.2; Cl, 12.1; N, 9.4. $C_{36}H_{24}Cl_2N_4$ requires C, 74.1; H, 4.15; Cl, 12.15; N, 9.6%). Reduction of the biphenylylazo-compound (3c), followed by chromatography on silica gel using 5% ether–petroleum as eluant, afforded bicarbazol-9-yl (18a) (5%), m.p. 224—226 °C; further elution gave 2-(*carbazol*-9-*ylamino*)*biphenyl* (19a) (34%), m.p. 250—252 °C, $\nu_{max.}$ 3 330 $cm^{-1}$ (NH), *m/e* 334 ($M^+$), 169, 168, 167, 166, 140, and 139, $\lambda_{max.}$ 233, 292, 323, and 337 nm (log ε 4.65, 4.29, 3.63, and 3.60) (Found: C, 86.0; H, 5.5; N, 8.25. $C_{24}H_{18}N_2$ requires C, 86.2; H, 5.4; N, 8.4%). Elution with 10% ether–petroleum afforded carbazole (8%), and finally elution with ether afforded a mixture of products which could not be identified. Reduction of the dimethylbiphenylylazo-compound (3d), followed by chromatography of the reaction mixture on silica gel using 5% ether–petroleum, yielded 1,3-*dimethylbicarbazol*-9-*yl* (18b) (6%), m.p. 201—203 °C, $\nu_{max.}$ 1 230, 1 215, 762, 741, and 718 $cm^{-1}$, $\lambda_{max.}$ 231, 290, 320, and 332 nm (log ε 4.85, 4.45, 3.85, and 3.92), *m/e* 360 ($M^+$), 194, and 167 (Found: C, 85.9; H, 5.6; N, 7.8. $C_{26}H_{20}N_2$ requires C, 86.6; H, 5.6; N, 7.8%); further elution afforded 3′,5′-*dimethyl*-2-(*carbazol*-9-*ylamino*)*biphenyl* (19b) (37%), m.p. 203—205 °C, $\nu_{max.}$ 3 335 $cm^{-1}$ (NH), $\lambda_{max.}$ 233, 292, 323, and 337 nm (log ε 4.68, 4.24, 3.62, and 3.59), *m/e* 362 ($M^+$), 195, 194, 180, and 166 (Found: C, 85.5; H, 6.1; N, 7.8. $C_{26}H_{22}N_2$ requires C, 86.15; H, 6.1; N, 7.7%). Elution with 10% ether–petroleum afforded carbazole (5%), and elution with ether furnished a mixture of products which could not be identified.

*Decomposition of* 1,2-*Dicarbazol*-9-*yl*-1,2-*di*-(4-*tolyl*)-*hydrazine* (5a).—Compound (5a) (1 g) was suspended in dry benzene (50 ml) and stirred at room temperature for 24 h, after which t.l.c. showed that complete decomposition had occurred. Removal of the excess of solvent left a residue which was chromatographed on silica gel. Elution with 3% ether–petroleum afforded trace amounts of 4,4′-dimethylazobenzene (10a); elution with 5% ether–petroleum gave N-*carbazol*-9-*yl*-4-*toluidine* (6a) (10%), m.p. 175—177 °C, $\nu_{max.}$ 3 330 $cm^{-1}$ (NH), *m/e* 272 ($M^+$), 271, 257, 167, 166, 140, and 139 (Found: C, 83.65; H, 5.8; N, 10.4. $C_{19}H_{16}N_2$ requires C, 83.8; H, 5.9; N, 10.3%); elution with 10% ether–petroleum afforded carbazole (8) (3%); elution with ether yielded 2,7-dimethylphenazine (9a) in trace amounts. Finally elution with carbon disulphide gave $N^1N^2$-*dicarbazol*-9-*yl*-4-*methyl*-$N^2$-(4-*tolyl*)-o-*phenylene*-*diamine* (7a) (75%), m.p. 138—140 °C (decomp.), $\nu_{max.}$ 3 340 $cm^{-1}$ (NH), *m/e* 374, 208, 167, 166, 140, and 139, δ($CS_2$) 2.1 (3 H, s), 2.31 (3 H, s), and 5.81—8.09 (23 H, m) (Found: C, 83.35; H, 5.6; N, 10.2. $C_{38}H_{30}N_4$ requires C, 84.1; H, 5.6; N, 10.3%).

*Decomposition of* 1,2-*Dicarbazol*-9-*yl*-1,2-*bis*-(4-*chlorophenyl*)*hydrazine* (5b).—Decomposition of compound (5b) was carried out as just described for compound (5a). Chromatography gave (a) trace amounts of 4,4′-dichloroazobenzene (10b); (b) N-*carbazol*-9-*yl*-4-*chloroaniline* (6b) (15%), m.p. 195—197 °C, $\nu_{max.}$ 3 325 $cm^{-1}$ (NH), *m/e* 292 ($M^+$), 291, 257, 255, 167, 166, 140, and 139 (Found: C, 73.95; H, 4.4; Cl, 12.3; N, 9.65. $C_{18}H_{13}ClN_2$ requires C, 73.85; H, 4.5; Cl, 12.1; N, 9.6%); (c) carbazole (8) (10%); (d) 2,7-dichlorophenazine (9b) (3%), and (e) $N^1N^2$-*dicarbazol*-9-*yl*-4-*chloro*-$N^2$-(4-*chlorophenyl*)-o-*phenylene*-*diamine* (7b) (60%), m.p. 213—215 °C (decomp.), $\nu_{max.}$ 3 340 $cm^{-1}$ (NH) (Found: C, 73.7; H, 4.15; Cl, 11.95; N, 9.4. $C_{36}H_{24}Cl_2N_4$ requires C, 74.1; H, 4.15; Cl, 12.15; N, 9.6%).

*Decomposition of the Diamine* (7a).—A solution of compound (7a) (200 mg, 0.37 mmol) in freshly degassed benzene (20 ml) was refluxed overnight; the excess of solvent was distilled off and the residue was chromatographed on a silica gel column. Elution with carbon disulphide afforded carbazole (8) (110 mg, 0.72 mmol, 97%). Elution with ether then gave 2,7-dimethylphenazine (9a) (75 mg, 0.36 mmol, 97%).

*Decomposition of the Diamine* (7b).—Compound (7b) (1 g, 1.7 mmol) was refluxed in degassed benzene (80 ml) for 15 h, after which t.l.c. showed complete absence of starting material and formation of carbazole (8) and 2,7-dichlorophenazine (9b). Removal of solvent and chromatography on silica gel gave carbazole (8) (0.55 g, 3.3 mmol, 97%) and 2,7-dichlorophenazine (9b) (0.40 g, 1.6 mmol, 94%).

*Cyclization of* 2-(*Carbazol*-9-*ylamino*)*biphenyl* (19a) *and* 3′,5′-*Dimethyl*-2-(*carbazol*-9-*ylamino*)*biphenyl* (19b).—Solutions of compounds (19a) and (19b) (2 mmol) in dry benzene (50 ml) containing *o*-chloranil (3 mmol) were refluxed for 10 h. Solvent was distilled off and the residue was chromatographed on a silica gel column, using 5% ether–petroleum as eluant. Quantitative yields of bicarbazol-9-yl (18a) and 1,3-dimethylbicarbazol-9-yl (18b) were obtained from (19a) and (19b) respectively.

Qualitative experiments showed that cyclization of (19a) and (19b) to (18a) and (18b) could be performed by treatment with lead dioxide or silver oxide in ether solution at room temperature. However in these cases t.l.c. showed formation of significant amounts of coloured products as well as the bicarbazolyls (19a) and (19b).

*Oxidation of* 2-(4-*Chlorophenyl*)-1,1-*diphenylhydrazine* (13).[4]—A mixture of the hydrazine (13) (1.1 g) in dry ether (50 ml) and lead dioxide (10 g) was stirred at room temperature for 16 h, after which t.l.c. showed that no starting material was left. The solution was filtered and the residue was washed with ether. The combined filtrate and washings were evaporated and the residue chromatographed on silica gel. Elution with 3% ether–petroleum gave 4,4′-dichloroazobenzene (10b) (6%); 5% ether–petroleum eluted tetraphenylhydrazine (9%) and diphenylamine (77%); ether eluted 2,7-dichlorophenazine (9b) (21%); further elution with ether gave a mixture of coloured products which could not be identified.

*Oxidation of* N-*Carbazol*-9-*yl*-4-*toluidine* (6a) *and* 4-*Chloro*-N-*carbazol*-9-*ylaniline* (6b).—Treatment of the arylamines (6a) and (6b) with lead dioxide in ether solution at room temperature led to the formation of carbazole (8), the phenazines (9a) and (9b), and considerable amounts of coloured material as revealed by t.l.c. analysis of the reaction mixtures. The presence of the diamines (7a) and (7b) was not detected by t.l.c., which also indicated the possible formation of the azobenzenes (10a) and (10b).

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