Gas Phase Rearrangement Reactions of 2-(Arylamino)phenylaminyl Radicals

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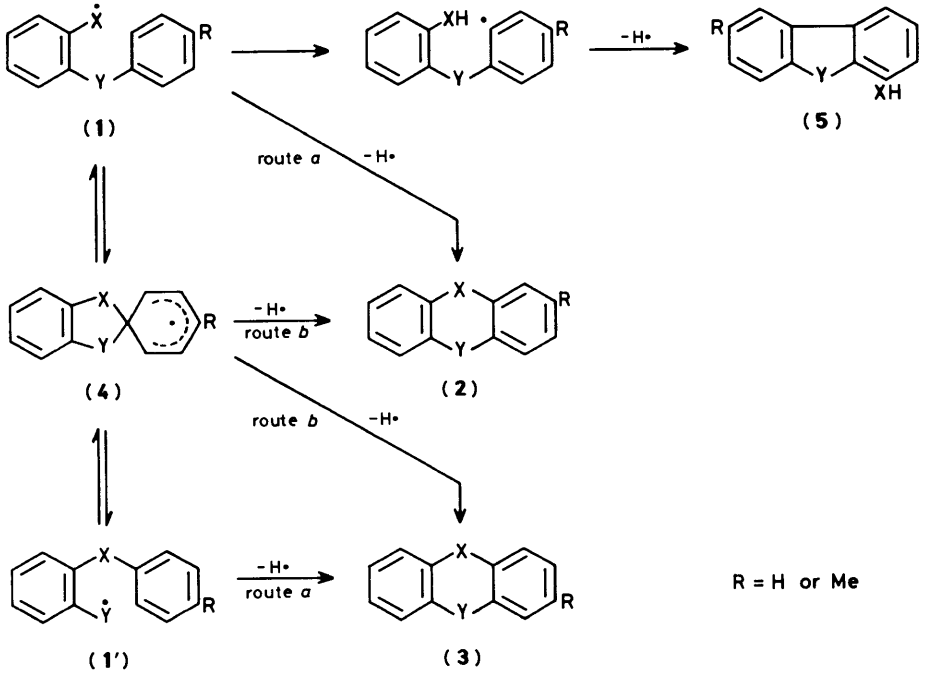
Generation of the aminyl radicals (**1**; X = Y = NH, R = H or Me) by flash vacuum pyrolysis leads to diphenylamines, phenazines, and aminocarbazoles. ^{15}N-Labelling studies have shown that the diphenylamine and phenazine products arise by equilibration of the initial aminyl radical *via* the spirodienyl radical (**4**; X = Y = NH).

We have recently described the gas-phase generation of arylaminyl radicals,[1] (and related benzyl and phenoxyl radicals) and their intramolecular reactions with *ortho* substituents which contain alkyl groups.[2–4] Our initial extension of this work to radicals with aryl-containing *ortho*-substituents[5] (**1**) revealed two new rearrangement processes *en route* to cyclisation products. The formation of the six-membered ring isomers (**2**) and (**3**) under dilute, low-pressure conditions is good evidence for the participation of a spirodienyl intermediate *e.g.* (**4**; X, Y = CH_2, O), reminiscent of related iminyl radical[6] and nitrene[7] reactions. The formation of the five-membered ring product *e.g.* (**5**; X = NH, Y = S) was, however, unprecedented,[5] and is thought to be due to hydrogen abstraction followed by cyclisation of the resulting aryl radical (Scheme 1). In the unsymmetrical cases (X ≠ Y) which we have reported,[5] a full interpretation of these results is not possible at this stage, due to unknown migration aptitudes in the spirodienyl (**4**) competing with unknown amounts of direct cyclisation [*e.g.* to (**2**) from (**1**)]. We have therefore sought to simplify this problem, and we present here full details of a symmetrical case (X = Y = NH) in which the participation of the spirodienyl is revealed by a ^{15}N labelling study, with analysis by ^{15}N n.m.r. spectroscopy.

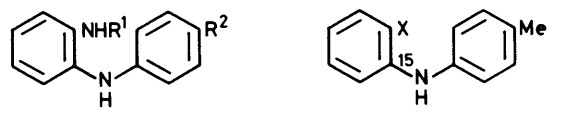
The *N*-allyl compounds (**8**), (**9**), and (**13**) which were the immediate precursors of the arylaminyl radicals,[1] were readily prepared in 40–50% yield by reaction of an excess of the appropriate amine (**6**), (**7**), or (**12**) with allyl bromide in dimethylformamide containing potassium carbonate. The proportions were optimised to minimise the formation of the *N*,*N*-diallyl derivative. The synthesis of the amines (**7**) and (**12**) was achieved by reduction of the nitro compounds (**14**) and (**11**), which were themselves obtained by treatment of 2-chloronitrobenzene with the anion of [^{14}N]- or [^{15}N]-4-methylformanilide respectively (Scheme 2). This method, which was originally applied to 4-nitrodiphenylamine derivatives,[8] was considered preferable to more conventional routes,[9,10] which require high temperatures, extended reaction times, and/or sealed tube conditions.

The [^{15}N] label was derived from [^{15}N]ammonium nitrate containing 5.6% excess of ^{15}N (*i.e. ca.* 15 times natural abundance), which was used to make [^{15}N]-*p*-toluidine as previously described.[6] Formylation under standard conditions (see the Experimental section) gave the required labelled formanilide.

Flash vacuum pyrolysis of the *N*-allyl compound (**8**) at 750 °C (10^{-3} Torr) gave a mixture of products, which could

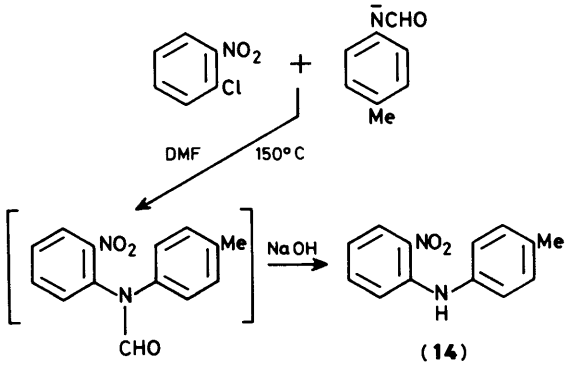


Scheme 1.



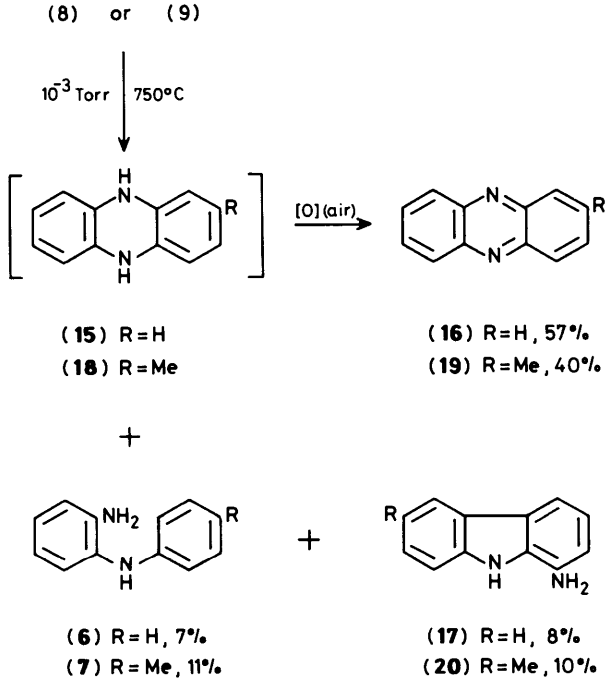
(6) $R^1 = R^2 = H$
(7) $R^1 = H$, $R^2 = Me$
(8) $R^1 = allyl$, $R^2 = H$
(9) $R^1 = allyl$, $R^2 = Me$
(10) $R^1 = COMe$, $R^2 = Me$

(11) $X = NO_2$
(12) $X = NH_2$
(13) $X = NHCH_2CH{=}CH_2$



Scheme 2.

be separated by chromatography on alumina (Scheme 3). The major product was the air-sensitive dihydrophenazine (**15**). which was always accompanied by some phenazine (**16**), formed either by thermal dehydrogenation, or by aerial oxidation on work-up. The analysis was therefore simplified by allowing the oxidation to take place (2—3 h in air at 20 °C) and isolating the phenazine (**16**), which was identical with an authentic sample.



(15) R = H
(18) R = Me
(16) R = H, 57%
(19) R = Me, 40%
(6) R = H, 7%
(7) R = Me, 11%
(17) R = H, 8%
(20) R = Me, 10%

Scheme 3.

A small amount of the amine (**6**) (7%) was also identified. Characterisation of the third product [*m/z* 182 (100%); 8% yield] was more difficult. Its ^1H n.m.r. spectrum showed the presence of just seven aromatic protons (confirmed by the presence of seven methine signals in the ^{13}C n.m.r. spectrum) together with signals at δ_H 10.84 (1 H) and at δ_H 5.16 (2 H) corresponding to an NH_2 group. The remaining five carbon atoms of the arylaminyl radical occur as quaternary signals in the ^{13}C n.m.r. spectrum. These data are consistent with the aminocarbazole structure (**17**) which would be formed by the rearrangement mechanism of Scheme 1 (R = H, X = Y = NH). The location of the amino substituent is confirmed by the literature m.p.s of the aminocarbazole isomers {observed m.p. 187—189 °C; [lit. (1-isomer[11]) 193 °C; (2-isomer[12]) 238 °C; (3-isomer[13]) 246—248 °C (decomp.); (4-isomer[14]) 188—192 °C]} and by calculation of the ^{13}C n.m.r. spectrum using the additivity effect[15] of the amino group (Table). This clearly distinguishes the 1- and 4-amino isomers. The correspondence between the observed and estimated values for the 1-isomer is well within 1 p.p.m., except in the region of the substituent (C-9a, C-1, and C-2) where steric effects are known to reduce the reliability of the method.[17] The absolute assignment may be ambiguous in certain cases (Table).

The detailed mechanism of the rearrangement to form (**17**) is not amenable to labelling studies, because of the rapid exchange of N*H* atoms, but the hydrogen transfer process of Scheme 1 remains consistent with the results of investigations on related systems which will be published in a later paper.

As expected, pyrolysis of the *p*-methyl-*N*-allyl derivative (**9**) yielded the appropriate methyl substituted phenazine (**19**) and amine (**7**) (Scheme 3) although these could only be separated by treatment of the mixture with acetic anhydride to give the *N*-acetyl compound (**21**), followed by chromatography. An authentic sample of 2-methylphenazine (**19**) was obtained, for comparison, by vapour-phase dehydrogenation of its tetrahydro derivative over palladium (0.5%) on alumina at 550 °C.[18,19] Insufficient of the carbazole (**20**) was obtained for full characterisation, though the location of the methyl group at the 6-position was confirmed by the appearance of the most deshielded aromatic signal in the ^1H n.m.r. spectrum (H-5) as a singlet.

In order to assess the involvement of the spirodienyl (**4**; X, Y = NH, ^{15}NH) from the pyrolysis of the specifically labelled compound (**13**) an analysis of the ^{15}N n.m.r. spectra of the phenazines (**16**) and (**19**), and the diphenylamine derivatives (**6**)

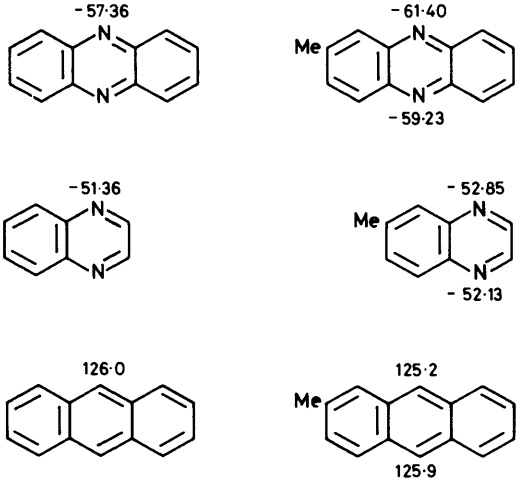
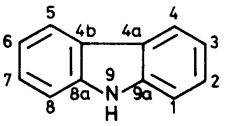


Figure 1. ^{15}N N.m.r. chemical shifts of phenazines and quinoxalines,[6] and ^{13}C n.m.r. chemical shifts of anthracenes[17]

Table. Observed and estimated ^{13}C n.m.r. chemical shifts (δ values) of 1-aminocarbazole



Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-4b	C-8a	C-9a
Carbazole[a]	110.99	125.54	118.54	120.17	120.17	118.54	125.54	110.99	122.51	122.51	139.81	139.81
1-Aminocarbazole[a] (observed)	133.39	109.34[e]	119.59[c]	108.35[e]	119.96	118.10	124.79	110.83[d]	123.22	122.71	139.10	128.78
1-Aminocarbazole (calculated)[b]	128.99	112.24	119.44	110.37	120.17	118.54	125.54	110.99	123.41	122.51	139.81	126.51
4-Aminocarbazole (calculated)	101.19	126.44	105.24	138.17	120.17	118.54	125.54	110.99	109.21	122.51	139.81	140.17

[a] $(CD_3)_2SO$ solution; [b] Estimated from the spectrum of carbazole assigned as in ref. 16 using the substituent effect of a 1-amino group; [c] Doublet in ^1H coupled ^{13}C n.m.r. spectrum; [d] Doublet of doublets in ^1H coupled ^{13}C n.m.r. spectrum, as found for carbazole itself; [e] Assignment may be reversed.

and (**7**) was carried out. Relative assignments of the two signals of the methylphenazine (**19**) (Figure 1) was made by comparison with the chemical shifts of related quinoxalines, which are known by unambiguous synthesis of mono-labelled derivatives,[6] and was confirmed by comparison with the ^{13}C n.m.r. chemical shifts of appropriate anthracenes.[20] For quaternary nitrogen atoms in comparable environments, triangulation of expanded peaks gives a consistent estimate of their relative areas.[6] In the present case, the relative areas of the 2-methylphenazine signals at δ_N −59.23 and −61.40 were 1.03:1.00.

The two signals of the 2-aminodiphenylamines (**6**) and (**7**) were distinguished, first, by a DEPT π/2 experiment which identified the NH signal of (**6**) (δ_N −304.63) and, second, by a DEPT π/3 experiment on the labelled derivative (**12**). This pulse sequence gives equal ehancement to NH and NH_2 signals, yet only the peak at δ_N −306.86 (corresponding to the labelled nitrogen atom) was present in the spectrum. The introduction of a *p*-methyl substituent is known to cause a low frequency shift in the ^{15}N n.m.r. spectra of aniline derivatives.[21] In both cases, the position of the NH_2 resonance was found by a broad band decoupled experiment using chromium tris(acetylacetonate) as relaxation reagent (Figure 2). Unfortunately, these conditions produced unreliable values for the relative sizes of the peaks, but the NH signal was generally larger than the NH_2 signal by a factor of 1.5—2.0.

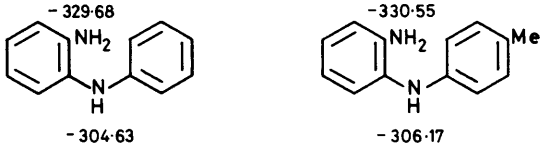


Figure 2. ^{15}N N.m.r. chemical shifts of the aminodiphenylamines (**6**) and (**7**)

Pyrolysis of the labelled derivative (**13**) under the standard conditions gave a dark pyrolysate which was mixed with [^2H]chloroform, and allowed to oxidise, as before. The small amount of labelled carbazole (**20**) obtained was insoluble under these conditions, and could not be analysed. The ^{15}N n.m.r. spectrum of the mixture therefore showed just four peaks, at δ_N −59.31 and −61.57 (ratio 1.04:1.00) corresponding to labelled phenazine (**19**), and at δ_N −306.17 and −330.55 (ratio *ca.* 1.5—2.7:1.0) corresponding to the labelled aminodiphenylamine (**7**). For the latter compound, the measurement of peak sizes is particularly approximate due to the high noise level and the low intensity of the NH_2 signal, but there is no doubt that both the NH and NH_2 sites are labelled.

The implications of these results for the mechanisms of Scheme 1 are as follows. First, the incorporation of label at both sites of the aminodiphenylamine (**7**) establishes that hydrogen capture by the radical (**1**; X = Y = NH) takes place predominantly (and perhaps exclusively) after equilibration *via* the spirodienyl (**4**; X = Y = NH). Hence, we have established that the spirodienyl (**4**), once formed, is capable of reverting to the ring-opened forms (**1**) or (**1′**). Second, the two sites of the 2-methylphenazine (**19**) obtained by pyrolysis of (**13**) are, within experimental error, equally labelled with ^{15}N (±1%). Hence the spirodienyl (**4**; X = Y = NH) is an essential intermediate *en route* to the phenazine, which is not formed to any significant extent by direct cyclisation of the aminyl (**1**; X = Y = NH). These results are in contrast to the iminyl case,[6] in which direct cyclisation can account for up to 30% of the reaction pathway. Our present work does not allow a distinction between two possible cyclisation mechanisms (Scheme 1), either by re-cyclisation of the interconverted aminyl radicals (**1**) and (**1′**) (Route a) or by sigmatropic migration from the spirodienyl itself (Route b). We hope to comment on these possibilities for a related example, in a later paper.

Experimental

Unless otherwise stated, ^1H n.m.r. spectra were recorded at 80 or 200 MHz for solutions in [^2H]chloroform; ^{13}C and ^{15}N n.m.r. spectra were recorded at 20 and 36.5 MHz respectively, also for solutions in [^2H]chloroform. ^{15}N N.m.r. chemical shifts are quoted with reference to external nitromethane; positive shifts are to high frequency.

2-(*Allylamino*)*diphenylamine* (**8**).—A mixture of 2-aminodiphenylamine (5.0 g, 27 mmol), allyl bromide (2.8 g, 23 mmol), potassium carbonate (3.2 g, 23 mmol) and dimethylformamide (DMF) (65 ml) was stirred vigorously for 23 h at room temperature. The excess of potassium carbonate was filtered off, water (100 ml) was added to the filtrate, and the solution was extracted with ether (3 × 100 ml). The combined organic layers were washed with water (3 × 100 ml), dried ($MgSO_4$) and the solvent was removed under reduced pressure to give an oil (4.60 g), which was a mixture of the 2-(allylamino) and 2-(diallylamino) derivatives, together with some recovered starting material. The required mono-allyl compound was obtained as the central fraction, by column chromatography on 6% deactivated alumina, using light petroleum (b.p. 40—60 °C)–ether (80:20) as eluant. Final purification by bulb-to-bulb distillation gave 2-(*allylamino*)*diphenylamine* (2.73 g, 53%), b.p.

148—150 °C (0.5 Torr) (Found: C, 80.35; H, 6.95; N, 12.4. $C_{15}H_{16}N_2$ requires C, 80.3; H, 7.2; N, 12.5%); δ_H 6.64–7.35 (9 H, m), 6.00 (1 H, m), 5.0—5.5 (3 H, m), 4.23 (1 H, br s), and 3.85 (2 H, m); δ_C 145.72 (q), 143.86 (q), 135.32, 129.15, 128.09 (q), 126.09, 124.96, 119.15, 117.25, 115.89, 115.13, 111.29, and 46.17; *m/z* 224 (M^+, 63%), 195 (88), 183 (59), 182 (100), 105 (31), and 77 (38).

2-*Nitro*-4′-*methyldiphenylamine* (**14**).—(*cf.* reference 8) Toluene (25 ml) was heated under nitrogen (heating mantle) in an oven-dried round bottomed flask fitted with a thermometer, a dropping funnel, a mechanical stirrer (glass blade) and a condenser. Sodium (0.8 g, 35 mmol) was added in large pieces down the condenser, with vigorous stirring, and the temperature of the toluene was increased to 100 °C to melt the sodium. Molten 4-methylformanilide (5.0 g, 37 mmol) was then added, with stirring, as rapidly as possible, *via* the dropping funnel. While still hot, the apparatus was re-assembled for distillation, and a solution of 2-nitrochlorobenzene (5.0 g, 31.7 mmol) in DMF (5 ml) was added in one portion and the temperature was further increased so that the toluene distilled off. The temperature rose to about 150 °C, whereupon the reaction became exothermic, but was readily controlled by removal of the heating mantle when necessary. The temperature was maintained at 150—155 °C for 2 h, after which the DMF was removed by distillation, and sodium hydroxide solution (30%, 5 ml) was added to the warm residue. The hydrolysis of the excess formanilide was completed during steam distillation (*ca.* 50 ml distillate collected), to remove *p*-toluidine and unchanged 2-nitrochlorobenzene. The cooled residue was extracted with methylene dichloride (2 × 50 ml), the combined organic layers were washed with water (50 ml), dried ($MgSO_4$), and the solvent was removed under reduced pressure. The black oil which was obtained was purified by bulb-to-bulb distillation to give the nitro compound as a red solid (4.15 g, 57%), m.p. 64—65 °C (lit.,[9] 69—70 °C), δ_H 9.42 (1 H, br s), 8.19 (1 H, dd), 6.0—7.45 (6 H, m), 6.72 (1 H, m), and 2.37 (3 H, s); δ_C 143.51 (q), 135.78 (q), 135.46, 132.70 (q), 130.13, 126.43, 124.62, 116.90, 115.78, and 20.81 (one quaternary signal is not apparent).

2-*Amino*-4′-*methyldiphenylamine*.—Palladium–charcoal (5%, 300 mg) was suspended in water (25 ml) and a solution of sodium borohydride (4.0 g, 0.11 mol) was added.[22] A slow stream of nitrogen was bubbled through the mixture, and a solution of 2-nitro-4′-methyldiphenylamine (4.10 g, 18 mmol) in the minimum amount of methanol (*ca.* 200 ml) was added dropwise. The reaction mixture was stirred at room temperature overnight and was then filtered to remove catalyst. The filtrate was acidified to destroy any excess of sodium borohydride, and was finally made basic (NaOH). It was then extracted with ether (3 × 200 ml), and the organic extracts were dried ($MgSO_4$) and concentrated to leave the amine (1.07 g, 31%), b.p. 123 °C (0.3 Torr), which was not, however, obtained in crystalline form [lit.,[9] m.p. 77 °C]; δ_H 6.5—7.5 (8 H, m), 5.0 (1 H, br s), 3.5 (2 H, br s), and 2.27 (3 H, s); δ_C 142.59 (q), 141.21 (q), 129.62, 128.68 (q), 124.92, 123.75, 119.01, 116.00, 115.67, and 20.31, (one quaternary signal is not apparent).

2-*Allylamino*-4′-*methyldiphenylamine* (**9**).—A mixture of 2-amino-4′-methyldiphenylamine (1.07 g, 5.4 mmol), allyl bromide (0.60 g, 5 mmol), potassium carbonate (0.69 g, 5 mmol) and DMF (25 ml) was stirred vigorously at room temperature for 48 h. The standard work-up, as described above for 2-(allylamino)diphenylamine, gave an oil (1.18 g) from which the required *allylamino compound* (0.51 g, 40%) was isolated after column chromatography [6% deactivated alumina, gradient elution with light petroleum (b.p. 40—60 °C)–ether (90:10—40:60)], b.p. 175—178 °C (0.3 Torr), (Found: M^+, 238.1484; $C_{16}H_{18}N_2$ requires M^+, 238.1470); δ_H 6.55—6.9 (4 H, m), 7.0—7.25 (4 H, m), 6.0 (1 H, m), 5.05—5.45 (2 H, m), 5.0 (1 H, br s), 4.18 (1 H, br s), 3.82 (2 H, m), and 2.32 (3 H, s); δ_C 143.38 (q), 143.06 (q), 135.35, 129.66, 128.97 (q), 128.67 (q), 125.53, 124.04, 117.31, 115.91, 115.64, 111.29, 46.24, and 20.38; *m/z* 238 (M^+, 50%), 209 (68), 194 (21), and 182 (100).

2-*Methylphenazine* (**19**).—Standard methods of dehydrogenation of 2-methyl-5,6,7,8-tetrahydrophenazine[23] were unsatisfactory but a moderate yield could be obtained using gas phase techniques. Thus the central part of a silica pyrolysis tube (35 × 2.5 cm) was packed with pellets of palladium (0.5%) on alumina, which were conditioned under vacuum at 550 °C for 3 h. 2-Methyl-5,6,7,8-tetrahydrophenazine[23] (0.92 g, 5 mmol) was distilled (140 °C, 0.01–0.6 Torr) through the furnace tube (2.5 h) to give a yellow crystalline pyrolysate (0.51 g). Separation of 2-methylphenazine from unchanged tetrahydro compound was achieved by column chromatography (6% deactivated alumina, chloroform). It was obtained in 53% yield, m.p. 114—115 °C [from light petroleum (b.p. 40—60 °C)] (lit.,[23] 117 °C), δ_H 8.1—8.3 (3 H, m), 7.99 (1 H, s), 7.75—7.9 (2 H, m), 7.67 (1 H, dd), and 2.65 (3 H, s); δ_C 143.51 (q), 143.36 (q), 142.88 (q), 142.21 (q), 141.01 (q), 133.34, 130.11, 129.71, 129.48, 129.41, 128.98, 127.55, and 22.07.

[1-^{15}N]-2-*Allylamino*-4′-*methyldiphenylamine*.—(a) [^{15}N]-4-*methylformanilide*. (*p*-Toluidine, containing *ca.* 5% N enrichment, was made by the Hofmann reaction as previously described[6]). A solution of formamide (1.09 g, 24 mmol), and [^{15}N]-*p*-toluidine (2.21 g, 18.6 mmol) in acetic acid (3.24 g) was heated at 60 °C for 1 h. The mixture was cooled, was added to water (20 ml), and was treated with aqueous sodium carbonate (10%; 20 ml). After extraction with methylene dichloride (4 × 25 ml) the combined organic layers were dried ($MgSO_4$) and concentrated to leave an oil which crystallised on trituration with ether. Recrystallisation from benzene–cyclohexane (20:80) gave the pure amide, which was obtained in 91% yield.

(b) [1-^{15}N]-2-*Nitro*-4′-*methyldiphenylamine* (**11**). This reaction was carried out using the formanilide from (a), on exactly one half of the scale described above for the unlabelled compound. The reaction was more difficult to control on a small scale and very impure product was obtained which could not be purified by distillation. However, column chromatography on 6% deactivated alumina using ether–light petroleum (b.p. 40—60 °C) (50:50) as eluant gave the pure nitro compound (0.46 g, 13%).

(c) [1-^{15}N]-2-*Amino*-4′-*methyldiphenylamine* (**12**). Reduction of the nitro compound (0.38 g, 1.7 mmol) from (b) using $NaBH_4$/Pd–C was more efficient than described above for the unlabelled compound, probably because problems of solubility were less on the smaller scale. The yield of amine, which was used without purification, was (0.17 g, 50%).

(d) [1-^{15}N]-2-*Allylamino*-4′-*methyldiphenylamine* (**13**). Allylation of the above amino compound (0.15 g, 0.74 mmol) using allyl bromide and potassium carbonate in DMF (10 ml) as previously described for the unlabelled compound, gave the ^{15}N-labelled 2-allylamino derivative (0.07 g, 40%) after chromatography.

Pyrolysis of 2-*Allylaminodiphenylamine*.—2-Allylaminodiphenylamine (1.49 g, 6.7 mmol) was distilled at 100—120 °C and 10^{-3} Torr over a period of 2 h through the furnace tube (35 × 2.5 cm), which was maintained at 750 °C. The major products condensed at the exit point of the furnace: the volatile products were trapped in a U-tube surrounded by liquid nitrogen. The pyrolysate was dissolved in chloroform and was set aside for 2 h to allow aerial oxidation of the insoluble di-

hydrophenazine. Column chromatography on 6% deactivated alumina, with light petroleum (b.p. 40—60 °C)–ether (50:50) as eluant gave two components. The first to be eluted was phenazine (0.27 g, 21%), m.p. 174—175 °C (from acetic acid) mixed m.p. 175—176 °C (lit.,[24] 175—176 °C); δ_H 8.1—8.3 (4 H, m), and 7.2—7.9 (4 H, m); δ_C 143.28 (q), 130.19, and 129.46 [δ_C (authentic phenazine) (50 MHz) 143.29 (q), 130.19, and 129.47]. The second component was 2-aminodiphenylamine (0.10 g, 7%), b.p. 106—108 °C (0.4 Torr) which could not be crystallised, though its spectra were identical with those of authentic samples; δ_H 6.65—7.3 (9 H, m), 5.2 (1 H, br s), and 3.75 (2 H, br s); δ_C 145.25 (q), 141.83 (q), 129.18, 128.43 (q), 125.58, 124.79, 119.18, 119.01, 116.01, and 115.09 [δ_C (authentic sample) 145.23 (q), 141.83 (q), 129.15, 128.39 (q), 125.57, 124.78, 119.14, 118.97, 116.00, and 115.06]. Further elution of the column with methanol gave 1-aminocarbazole (0.19 g, 15%), m.p. 187—189 °C (lit.,[11] 193 °C); δ_H [$(CD_3)_2SO$; 200 MHz], 10.84 (1 H, s), 8.00 (1 H, d), 7.50 (1 H, d), 7.34 (2 H, m), 7.11 (1 H, t), 6.92 (1 H, t), 6.67 (1 H, d), and 5.16 (2 H, br s); δ_C [$(CD_3)_2SO$; 50 MHz] 139.10 (q), 133.39 (q), 128.78 (q), 124.79, 123.22 (q), 122.71 (q), 119.96, 119.59, 118.10, 110.83, 109.34, and 108.35; *m/z* 182 (M^+, 100%), 57 (22), and 55 (28). A repeat pyrolysis on a small scale (0.13 g, 0.56 mmol) under similar conditions with g.l.c. analysis of the products (5% SE30) using pyrene as internal standard, gave the following yields after correction for detector response, phenazine (57%), 2-aminodiphenylamine (7%), and 1-aminocarbazole (8%).

Pyrolysis of 2-Allylamino-4′-methyldiphenylamine (**9**).—The yields for this pyrolysis were estimated from the n.m.r. spectrum of a small-scale pyrolysate, using cyclohexane (5 μl) as integral standard. Thus the allyl compound (12 mg, 0.09 mmol) was distilled at 100 °C (10^{-3} Torr), during 40 min, through the furnace tube which was maintained at 750 °C. The pyrolysate, which was trapped by liquid nitrogen, was suspended in [^{2}H]chloroform, and allowed to oxidise in air until all the solid had dissolved. The n.m.r. spectrum showed 2-methylphenazine (40%), 1-amino-6-methylcarbazole (10%) and 2-amino-4′-methyldiphenylamine (11%), by comparison of the chemical shifts of their methyl protons with those of authentic (or isolated samples).

Pyrolysis of the allyl compound (0.27 g, 1.13 mmol) under similar conditions over 2.25 h gave a semi-solid pyrolysate which was suspended in chloroform and set aside in air until all the solid had dissolved. The solvent was removed and column chromatography of the residue [6% deactivated alumina, eluted with light petroleum (b.p. 40—60 °C)–ether, 60:40] gave a mixture of 2-methylphenazine and 2-amino-4′-methyldiphenylamine which could not be further separated by chromatography on silica or alumina. Further elution with methanol gave a small amount of impure 1-amino-6-methylcarbazole (15 mg, 7%), b.p. 89—92 °C (0.3 Torr) (Found: M^+, 196.1000; $C_{13}H_{12}N$ requires M^+, 196.1000); δ_H[$(CD_3)_2CO$] 7.87 (1 H, s), 7.76 (1 H, d), 7.37 (1 H, d), 7.18 (1 H, d), 7.09 (1 H, t), 6.67 (1 H, d), and 2.47 (3 H, s); *m/z* 196 (M^+, 100%), 182 (31), 122 (15), and 89 (60).

Separation of the above mixture of the phenazine and diphenylamine (0.157 g) was effected by acetylation of the diphenylamine using acetic anhydride (0.4 ml) at 100 °C (5 min). The cooled mixture was diluted with water (10 ml), basified (NaOH), and extracted with methylene dichloride (3 × 10 ml). The dried ($MgSO_4$) extracts were concentrated and chromatographed on 6% deactivated alumina (chloroform) to give 2-methylphenazine (93 mg, 42%) after sublimation at 88—90 °C (0.3 Torr), m.p. 114—116 °C [from light petroleum (b.p. 40—60 °C)], mixed m.p. 112—114 °C (lit.,[23] 117 °C), whose ^{1}H and ^{13}C n.m.r. spectra were identical with those of the authentic material. The second fraction from the column consisted of impure 2-acetylamino-4′-methyldiphenylamine (24 mg, 9%) (Found: M^+, 240.1262; $C_{15}H_{16}N_2O$ requires M^+, 240.1262); δ_H 6.6—7.8 (10 H, m), 2.26 (3 H, s), and 2.08 (3 H, s); *m/z* 240 (M^+, 95%), 222 (100), 198 (40), and 182 (45%).

Pyrolysis of [1-^{15}N]-2-*Allylamino-4′-methyldiphenylamine.*—Sublimation of the labelled diphenylamine (79 mg, 0.33 mmol) at 100 °C during 75 min into the standard furnace tube at 750 °C and 10^{-3} Torr, gave a pyrolysate which was suspended in [^{2}H]chloroform, and set aside in air until the solid had dissolved. This solution was used for the ^{15}N n.m.r. spectra, without further purification: the results are reported in the Discussion section.

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