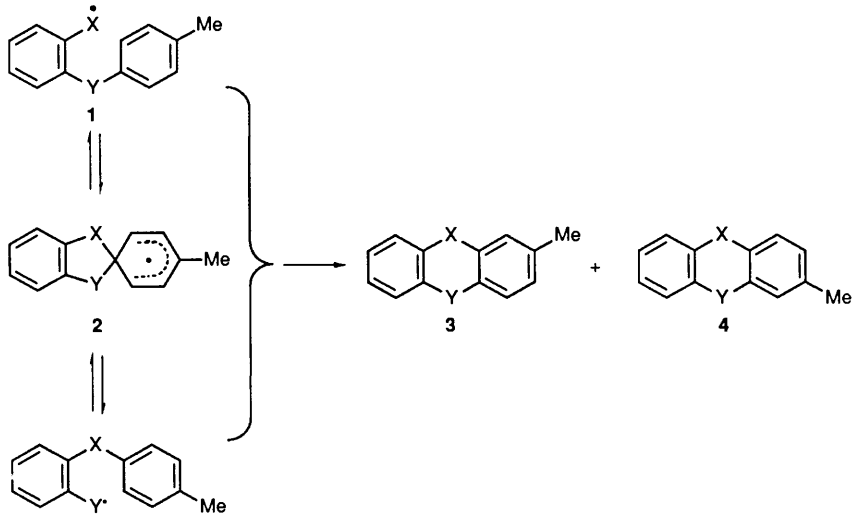
Gas-phase Rearrangement and Cyclisation Reactions of 2-Benzylphenylaminyl Radicals and Related 2-Hetero-analogues[1]

J. I. G. Cadogan,*[a] Clare L. Hickson,[b] H. Susan Hutchison[b] and Hamish McNab*[b]
[a] *BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN*
[b] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ*

Gas-phase pyrolysis of the appropriate *N*-allyl or *N*-benzyl compound leads to the aminyl radicals **1** (X = NH, Y = CH_2, CO, S, or O). Equilibration of these *via* the spirodienyl **2** gives mixtures of isomeric acridans or acridones as major products from radicals **1** (X = NH, Y = CH_2 and Y = CO, respectively) and isomeric phenothiazines as minor products from radical **1** (X = NH, Y = S). The major product in this case is the aminodibenzofuran **29** which may be formed by H-abstraction by the aminyl to give an aryl radical, followed by cyclisation (Scheme 6). The only cyclised product from radical **1** (X = NH, Y = O) is the carbazole **35**, formed by a mechanism similar to that of Scheme 6, but in which H-abstraction by the rearranged phenoxyl radical has taken place.

We have recently described the gas-phase generation, rearrangement, and cyclisation reactions of the *ortho*-substituted radicals **1** (X, Y = NH)[2] and **1** (X, Y = CH_2, S)[3] (Scheme 1). In both cases, equilibration *via* the spirodienyl **2** was essentially complete, leading to equal quantities of the isomeric products **3** and **4**. Here we report the gas-phase chemistry of a series of aminyl radicals **1** (X = NH) and the hitherto unsuspected influence of the heteroatom Y (CH_2, CO, S, O) on the course of such reactions.



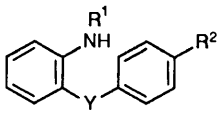
Scheme 1

Results and Discussion

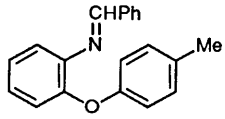
In all cases, the radicals were generated by flash vacuum pyrolysis of the appropriate *N*-allyl compound **6**, **8**, **10**, **12**, **14** or **16** at 750 °C (*ca.* 10^{-3} Torr).† These compounds were obtained by alkylation [allyl bromide, potassium carbonate, dimethylformamide (DMF)] of the corresponding aniline derivative, followed by chromatography on alumina; in turn, the anilines were either commercially available or were prepared by literature methods. Thus, 2-amino-4′-methylbenzophenone **11** was made by Friedel–Crafts acylation of toluene with *N*-tosylanthranilic acid chloride,[4] and the corresponding diphenylmethane **7** was obtained by Wolff–Kischner reduction.[3] Similarly, 2-aminodiphenylmethane **5**[5] was synthesized from the commercially available 2-aminobenzophenone **9**, whereas catalytic reduction of 2-nitro-4′-methyldiphenyl sulphide[6] or the corresponding ether[7] gave the 2-amino derivatives **13**[8] and **15**,[9] respectively. Condensation of the 2-phenoxyaniline **15** with benzaldehyde followed by sodium borohydride reduction[10] of the resulting imine **18** gave the *N*-benzyl derivative **17** as a crystalline solid. This was used as an alternative to the *N*-allyl compound as a source of the corresponding aminyl radical[11] (see below).

The mass spectra of all the *N*-allyl compounds studied show significant molecular ions, but the breakdown patterns are strongly dependent on the bridging heteroatoms (Y). Thus the diphenylmethanes **6** and **8** give base peaks at (M − 41), corresponding to the loss of the allyl group, as found for the corresponding *S*-allyl derivatives.[3] However, the closely related benzophenones **10** and **12** apparently ionise at the carbonyl function and undergo β-cleavage to give two complementary fragments, both of which may be detected [*e.g.*, **10**, *m/z* 237 (M^+, 100%) shows daughter ions at both *m/z* 105 (PhCO; 30%) and *m/z* 132 (36%)]. In contrast, the major fragmentation pathway from the molecular ions of the diphenyl sulphide **14** and the diphenyl ether **16** involves loss of the entire *NH*-allyl unit (56 amu) [*e.g.*, **16** *m/z* 239 (M^+, 100%), 183 (M − 56; 30%)].

† 1 Torr = 133.322 Pa.



	Y	R^1	R^2
5	CH_2	H	H
6	CH_2	allyl	H
7	CH_2	H	Me
8	CH_2	allyl	Me
9	CO	H	H
10	CO	allyl	H
11	CO	H	Me
12	CO	allyl	Me
13	S	H	Me
14	S	allyl	Me
15	O	H	Me
16	O	allyl	Me
17	O	CH_2Ph	Me



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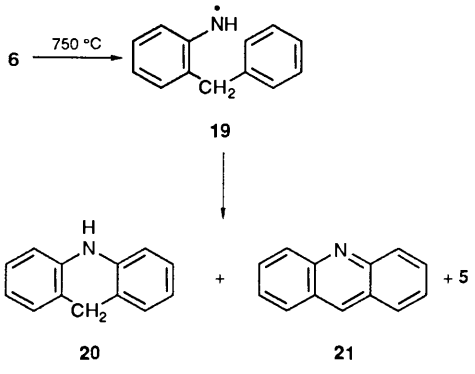
Generation of the aminyl radical **19** by flash pyrolysis of the allyl compound **6** resulted in the expected formation of acridan **20** (50%) together with small quantities of the amine **5** (8%) and acridine **21** (11%) (Scheme 2). The acridine certainly arises by dehydrogenation of acridan (though this may be a thermal or an aerial oxidation process), and the 2-aminodiphenylmethane **5** is probably formed by hydrogen capture of the radical **19**. These results are, in general, similar to those we have obtained for 2-arylaminophenylaminyls **1** (X = Y = NH).[2]



Scheme 2

A study of the methyl-labelled radical **22** first requires an unambiguous method for analysis of the two regioisomeric acridans **3** and **4** (X = NH, Y = CH_2) which could be obtained *via* the spirodienyl **2** (X = NH, Y = CH_2) (Schemes 1 and 3), and both the ^{15}N NMR and ^{13}C NMR methods which we have used previously[2,3] are applicable here. Thus, a comparison of the ^{15}N NMR spectra of acridan and an authentic sample of its 2-methyl derivative[12] shows that the substitution causes shielding of *ca.* 1.3 ppm (Fig. 1). A substantial shielding effect is also found for the corresponding simple aniline derivatives[13] (Fig. 1), for which *meta*-substitution causes a much smaller low-frequency shift. On this basis, the signal for 3-methylacridan would be predicted to occur close to that for acridan itself, at δ_N *ca.* −288.6.* Similarly, in the ^{13}C NMR spectra, the methyl group in 2- and 3-methylacridan causes a shielding effect at the methylene position of 0.04 and 0.45 ppm, respectively;[14] other regioisomers have substantially different effects.[14]

The crude pyrolysate from compound **8** showed two signals

* Shifts are quoted relative to external nitromethane.

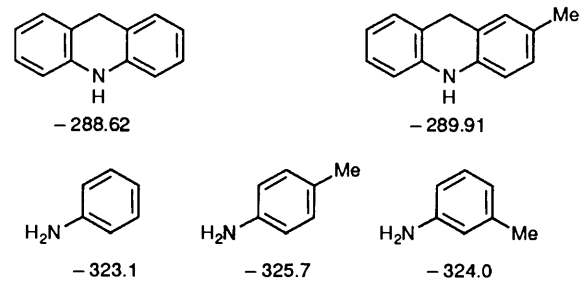
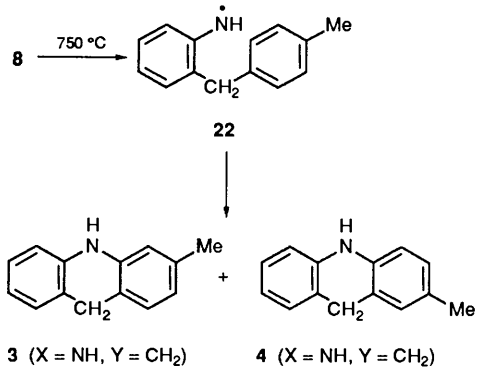


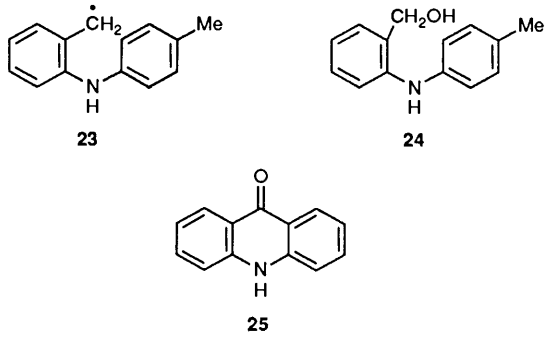
Fig. 1 ^{15}N NMR spectra of certain acridan and aniline[13] derivatives (chemical shifts in ppm relative to external nitromethane)



Scheme 3

in the ^{15}N NMR spectrum in the acridan region, at δ_N −290.08 and −288.95, and two signals in the acridan methylene region, at δ_C 31.23 and 30.83. In both cases, the ratio of the peaks was *ca.* 2:1. The first isomer clearly corresponds to 2-methylacridan **4** (X = NH, Y = CH_2) by comparison with an authentic sample, while the increased shielding (0.40 ppm) in the ^{13}C NMR spectrum serves to identify the second compound as the 3-methyl isomer: the ^{15}N NMR signal at δ_N −288.95 is also consistent with this interpretation.

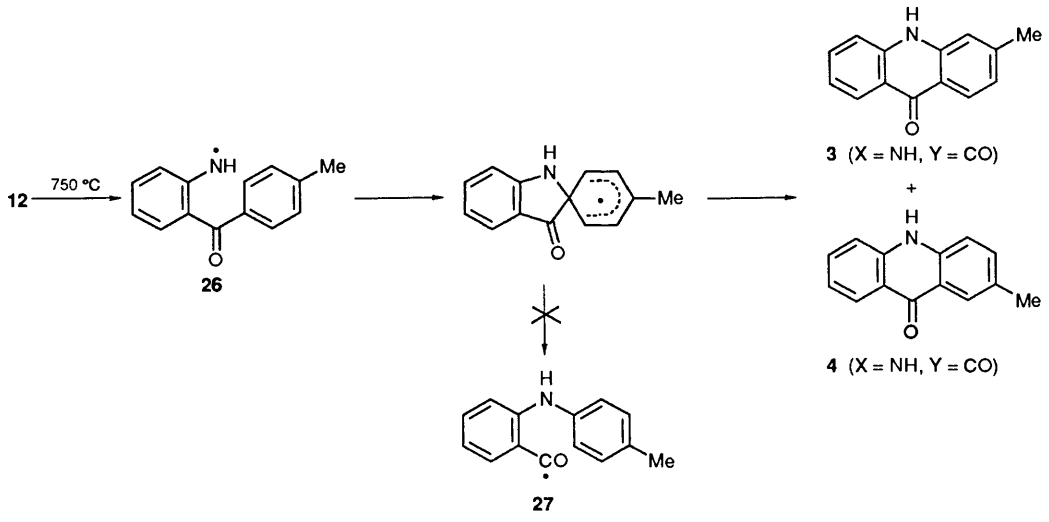
Hence, it is clear that the aminyl radical **22** cyclises by rearrangement *via* the spirodienyl **2** (X = NH, Y = CH_2) and that CH_2 migration rather than NH migration is preferred. This result is surprising, since related work on vinyl/iminyl[15,16] and amidyl[17,18] migration has shown that nitrogen- rather than carbon-atom migration is favoured in most cases. Unfortunately, attempts to confirm this result by generation of the complementary benzyl radical **23** *via* the oxalate[19] were unsuccessful, since the benzyl alcohol **24** did not form an oxalate derivative under standard conditions.[20]



23 **24**

25

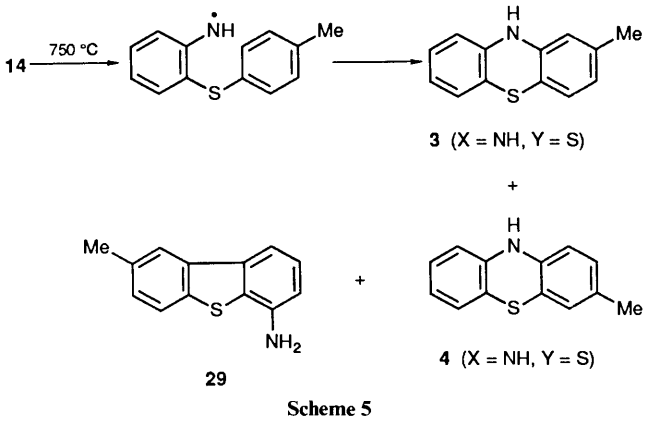
2-Allylaminobenzophenone **10** undergoes a particularly clean reaction on pyrolysis at 750 °C (10^{-3} Torr), with the formation of acridone **25** as the only significant product, in *ca.* 80% yield. Under the same conditions, the *para*-methyl



Scheme 4

derivative **12** also gave a yellow, highly crystalline, involatile pyrolysate, but whose NMR spectra showed the presence of *two* methyl groups (δ_H 2.40 and 2.37; δ_C 21.43 and 20.47) and *two* carbonyl groups (δ_C 176.60 and 176.50), in essentially 1:1 ratio (51:49). Identification of the peaks at δ_C 21.43 and 176.50 as being due to 3-methylacridone **3** (X = NH, Y = CO) and those at δ_C 20.47 and 176.60 as being due to 2-methylacridone **4** (X = NH, Y = CO) follows from the literature[21] (3-methyl isomer δ_C 21.6 and 176.4; 2-methyl isomer δ_C 20.4 and 176.5) which also serves to exclude the 1- and 4-methyl derivatives (δ_C 23.8 and 178.6; 17.9 and 177.4, respectively). It appears, therefore, that collapse of the aminyl **26** to the spirodienyl **2** (X = NH, Y = CO) is followed by essentially equal migration of NH and CO groups to give the observed product mixture (Scheme 4). Two other points are noteworthy. First, the formation of the mixture of acridone isomers excludes a feasible non-radical mechanism similar to that of Boekelheide for the cyclisation of *N*-arylanthranilate esters.[22] Second, the absence of side products—in particular carbazoles—in these reactions apparently excludes the possibility of ring opening of the spirodienyl to give the acyl radical **27**: there is good evidence that such species would be expected to decarbonylate at 750 °C.[23,24]

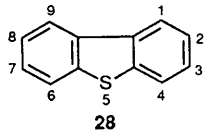
In contrast to these relatively straightforward reactions, pyrolysis of the diaryl sulphide **14** gave a complex mixture, but two major components could be isolated by chromatography on alumina (Scheme 5). The first component consisted of a



Scheme 5

mixture of two phenothiazines, identified as the 2- and 3-methyl isomers **3** and **4** (X = NH, Y = S) by comparison of their ^1H and ^{13}C NMR spectra with those of authentic (or related) samples (Table 1) (see also Experimental section). As found for the diphenylmethane case (above), the isomer present in greater amount was the rearranged 3-methyl derivative **4** (X = NH, Y = S), which suggests that S has a greater migrating aptitude than NH from the corresponding spirodienyl **2**. These results are consistent with our earlier work, which has shown that S and CH_2 have similar migratory aptitudes in these systems.[3]

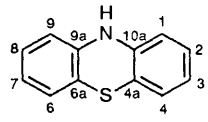
The major component of the pyrolysate (*ca.* 34%), though isomeric with the phenothiazines (*m/z* 213), showed only six aromatic protons in its ^1H NMR spectrum, together with a methyl group and an amino substituent. These data are consistent with the structure being a disubstituted dibenzothiophene **28**. The signals due to the ring containing the methyl group can be identified since some 4-bond coupling from the adjacent ring protons to the methyl group is observed. Because one of these protons (at δ_H 7.92) is the *only singlet* in the aromatic region of the spectrum, it follows that the methyl group must be at the 7- or 8-position of the dibenzothiophene, and that the amino substituent must be in the *other* benzenoid ring. This ring shows three adjacent, mutually coupled protons (^3J 7.7 and ^4J 1.0 Hz), and so the amino group must be located at the 1- or 4-position. The remaining ambiguities were resolved by estimation of the ^{13}C NMR spectrum of the four possible products by additivity effects[26] (Table 2), and it can be seen that only the 4-amino-8-methyl isomer **29** gives a good fit to the experimental data.



This surprising pyrolysis behaviour has some generality since related materials have been obtained in low yield from 2-arylaminoaminyls,[2] and as the major product from 2-benzylphenoxyls[1,23] and 2-phenoxyaminyls (see below). The formation of these rearrangement products may be *rationalised* by the hydrogen-abstraction pathway shown in Scheme 6, which is discussed further in the following paper.[23] The specificity of the process is particularly unusual: the mercaptocarbazole **30**, which might be expected to arise by a similar process, is clearly absent. Similarly, trace amounts of the amine **13** were detected, but there is no evidence for the presence of the thiol **31** in the pyrolysate.

Pyrolysis of the 2-allylaminodiphenyl ether **16** gave a complex, dark-coloured pyrolysate from which only 2-(*p*-toluidino)-phenol **32** (20%) was isolated and identified with certainty. This

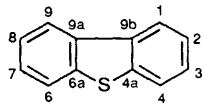
Table 1 ^{13}C NMR chemical shifts of some methylated phenothiazines



	C-1	C-2	C-3	C-4	C-4a	C-6	C-6a	C-7	C-8	C-9	C-9a	C-10a
Authentic 3-methylphenothiazine[a]	114.30	126.48	130.66	127.42	116.38	126.21	116.38	121.42	127.93	114.30	142.42	139.59
Major component of isolated fraction[a]	114.28	126.45	130.68	127.42	116.26	126.19	116.26	121.42	127.94	114.28	142.36	139.56
Authentic 2,7-dimethylphenothiazine[a,b]	115.00	136.79	122.18	126.01	113.00	127.85	116.16	130.54	126.48	114.32	139.68	142.35
Minor component of isolated fraction[a]	115.11	136.88	122.47	126.01	112.71	——— same as major component ———						142.02
2-Methylphenothiazine (calculated values)[c]	115.1	136.6	122.4	126.0	113.3	126.0	116.2	121.6	127.3	114.3	142.0	142.0

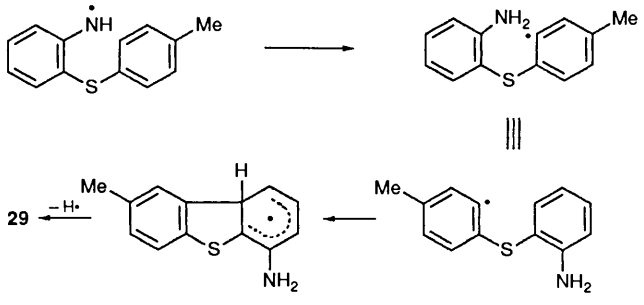
[a] [$^2H_6$]DMSO solution. [b] Ref. 25. [c] Calculated using substituent effect of methyl group.[26]

Table 2 Observed and estimated ^{13}C NMR chemical shifts of some aminomethyldibenzothiophenes

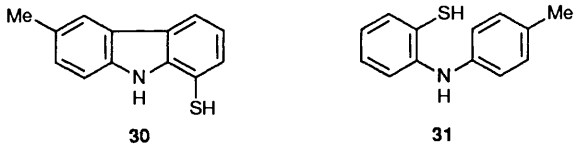


	C-1	C-2	C-3	C-4	C-6	C-7	C-8	C-9	C-4a	C-9b	C-9a	C-6a
Compound isolated from pyrolysate[a]	111.18	125.51	112.34	140.86	122.44	128.02	134.09	122.11	125.94	136.53	135.64	136.53
4-Amino-8-methyldibenzothiophene[b]	111.5	124.9	113.0	140.4	122.4	127.1	133.3	122.1	126.0	136.2	135.3	136.4
4-Amino-7-methyldibenzothiophene[b]	118.4	124.0	125.5	131.7	123.3	113.0	142.0	108.0	140.1	135.3	136.2	129.5
1-Amino-8-methyldibenzothiophene[b]	112.0	124.8	126.3	119.5	109.1	144.3	110.7	122.2	139.3	136.1	125.5	138.4
1-Amino-7-methyldibenzothiophene[b]	139.3	110.7	127.2	112.6	123.6	135.6	124.8	121.3	126.0	136.2	132.4	139.3

[a] [^2H]Chloroform solution. [b] Based on data for dibenzothiophene[27] and the additivity effect of methyl and of amino groups in benzenoid systems.[26]



Scheme 6

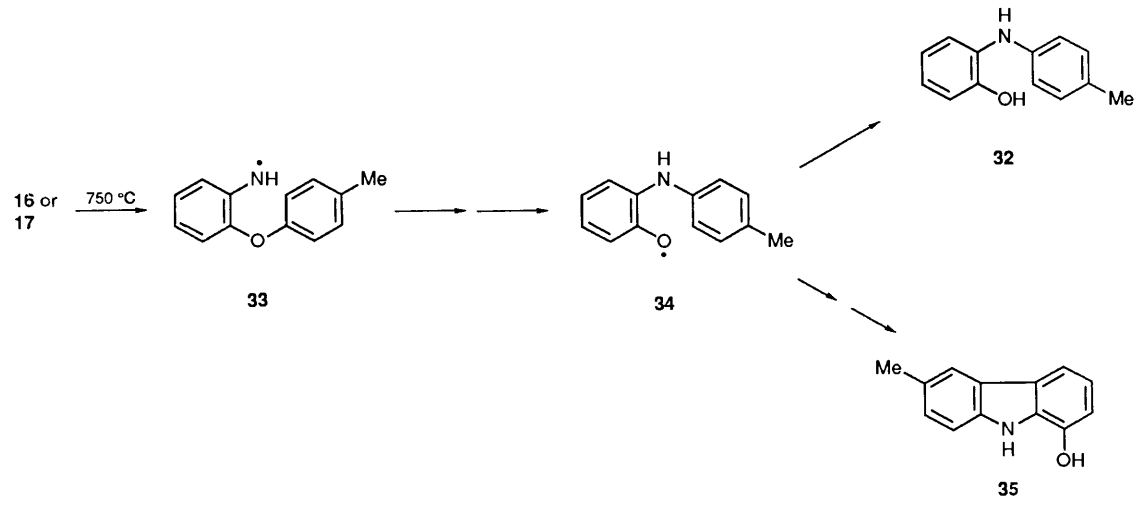


30 **31**

product is presumably formed by isomerisation of the aminyl **33** to the phenoxyl **34** *via* the spirodienyl radical **2** (X = NH, Y = O), followed by hydrogen-atom capture (Scheme 7). Since we have found that pyrolysis of benzyl derivatives gives rise to a smaller hydrogen-atom flux than does that of the corresponding allyl compound,[23] we synthesized and pyrolysed the *N*-benzyl derivative **17** in an attempt to minimise the formation of the phenol **32**. The pyrolysate which was obtained was rinsed from the trap with chloroform, which left an involatile grey solid (28% by weight). The chloroform fraction was extracted successively with acid and base. The acid-soluble fraction (5% by weight) was chiefly *p*-toluidine, presumably formed by aryl migration and subsequent cleavage. The NMR spectrum of the basic fraction (28% by weight) showed two major products characterised by methyl signals at δ_H([$^2H_6$]acetone) 2.26 and 2.50. The first of these was due to the phenol **32**, whereas the second was in the same position as that of the grey solid and that of the chief unidentified product from the pyrolysis of the allyl compound **16**. The neutral fraction (36% by weight) was chiefly bibenzyl [$\delta_H(CDCl_3)$ 3.14].

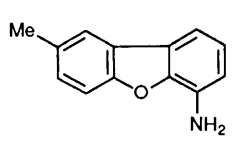
The grey solid was identified as the carbazole **35** by its chemical and spectroscopic properties. As with the related dibenzothiophene structure **29**, its ^{13}C NMR spectrum shows just six methine signals in the sp^2-hybridised region, which suggests that a new carbon–carbon bond has been formed. The corresponding ^1H signals are all well resolved at 200 MHz, and resonate as one singlet, one triplet and four doublets, which is the expected first-order coupling pattern from **35**: broad signals due to the NH and OH are located at δ_H([$^2H_6$]acetone) 10.01 and 8.58. The assignment was confirmed, as above, by ^{13}C NMR additivity effects using the reported spectrum of 1-hydroxycarbazole[28] as the basis for the estimation (Table 3). The isomeric dibenzofuran structure **36** was excluded because the isolated product is soluble in base and not in acid. The formation of compound **35** may follow a similar mechanism to that of Scheme 6 (see also the following paper[23]). The previously known[29] carbazole **35** was also identified retrospectively by comparison of ^1H NMR spectra as a component of the pyrolysate from the *N*-allyl derivative **16**.

Although not positively identified, the upper limits of formation of the amine **15**, the dibenzofuran **36**, and the phen-



Scheme 7

oxazines **37** may be estimated from ^{1}H NMR spectra. Peaks at δ_H 2.33 and 2.52 in the spectrum of the acid extract may be tentatively assigned to the methyl groups of compounds **15** and **36** respectively: the estimated yields are *ca.* 0.9 and 0.3%. The chemical shift of the aromatic protons of methylphenoxazine would be expected [30] to be δ_H *ca.* 6.5: if the observed broad, low-intensity peaks in this region of the spectrum of the crude pyrolysate are indeed due to phenoxazines, the yield is <2%.



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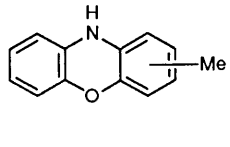

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A number of important features emerge from these results. First, hydrogen capture by O• (to give species **32**) is favoured over hydrogen capture by NH• (to give species **15**) by a factor of at least 25:1. Similarly, the rearrangement products **35** and **36** are generated overwhelmingly *via* hydrogen abstraction by the phenoxyl **34** rather than the aminyl **33**, even though it is the aminyl which is formed initially *and* it is hydrogen abstraction by the corresponding aminyl which leads to the dibenzothiophene **29**. Finally, the low level (if present) of the cyclisation products **3** and **4** is in marked contrast with the results of other aminyls reported in this and previous papers.[2]

In conclusion, we have shown that spirodienyls **2** are involved in the majority of the reactions of the aminyls **1** (X = NH, Y = CH_2, CO, S and O). In all cases (except Y = O), the cyclised products **3** and **4** are formed, and their relative proportion allows the assignment of migratory aptitude of the heteroatoms as CH_2, S > NH, CO. Ring opening of the spirodienyl followed by hydrogen-atom capture gives a major product from radical **1** (X = NH, Y = O), and phenoxyl radicals in particular seem prone to this behaviour.[1,23] The formation of the rearrangement products **29** [from radical **1** (X = NH, Y = S)] and **35** [from **1** (X = NH, Y = O)] are anomalous, and it is unclear at this stage just what factors are responsible for this marked and unusual change in behaviour. Experiments designed to clarify this situation for the related cases of radicals **1** (X = O, Y = CH_2, CO) are presented in the following paper.[23]

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 80 or 200 MHz, and 20 or 50 MHz respectively, for solutions in [^{2}H]chloroform, unless otherwise stated.

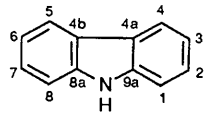
2-Allylaminodiphenylmethane and Related Heteroanalogues.—The appropriate amine (0.02 mol) was added to a solution of allyl bromide (0.015 mol) in DMF (50 cm^3) containing potassium carbonate (0.015 mol) as previously described.[2] The resulting mixture of starting material, *N*-allyl compound, and a small amount of the *N,N*-diallyl derivative was separated by chromatography on 6% deactivated alumina with 20% diethyl ether in light petroleum (40:60) as eluant. Fractions from the column were monitored by GLC. The fractions containing the required product were combined, the solvent was removed, and the remaining material was purified by distillation or recrystallisation. The following compounds were prepared by this method: *2-Allylaminodiphenylmethane* **6** (stirred for 16 h) (43%), b.p. 130–135 °C (0.2 Torr) (Found: C, 86.15; H, 7.7; N, 6.15. $C_{16}H_{17}N$ requires C, 86.05; H, 7.65; N, 6.25%); δ_H 7.05–7.35 (7 H, m), 6.63–6.78 (2 H, m), 5.84 (1 H, m), 5.05–5.15 (2 H, m), 3.92 (2 H, s), 3.72 (2 H, m), and 3.70 (1 H, br s); δ_C 145.73 (q), 139.14 (q), 135.09, 130.45, 128.45, 128.35, 127.60, 126.21, 124.52 (q), 117.06, 115.61, 110.78, 45.99, and 37.97; *m/z* 223 (M$^+$, 36%), 194 (9), 183 (15), 182 (100), 180 (18), 167 (9), 165 (15), and 91 (15).

2-Allylamino-4′-methyldiphenylmethane **8** (from 2-amino-4′-methyldiphenylmethane[3]) as a yellow oil (0.77 g, 52%), b.p. 160–162 °C (0.5 Torr) (Found: C, 85.9; H, 7.95; N, 5.7. $C_{17}H_{19}N$ requires C, 86.05; H, 8.0; N, 5.9%); δ_H 7.15–7.49 (6 H, m), 6.73–6.96 (2 H, m), 5.95 (1 H, m), 5.12–5.35 (2 H, m) 3.99 (2 H, s), 3.83 (2 H, m), 3.78 (1 H, br s) and 2.46 (3 H, s); δ_C 145.76 (q), 136.00 (q), 135.71 (q), 135.17, 130.39, 129.17, 128.15, 127.51, 124.82 (q), 117.05, 115.63, 110.78, 46.06, 37.57 and 20.86; *m/z* 237 (M$^+$, 37%), 210 (48), 196 (100), 181 (20) and 180 (26).

2-Allylaminobenzophenone **10** (stirred for 64 h) (49%), m.p. 53 °C (from EtOH) (Found: C, 81.05; H, 6.25; N, 6.05. $C_{16}H_{15}NO$ requires C, 81.0; H, 6.35; N, 5.9%); δ_H 8.75 (1 H, br s), 7.25–7.69 (7 H, m), 6.44–6.82 (2 H, m), 5.99 (1 H, m), 5.13–5.48 (2 H, m) and 3.95 (2 H, m); δ_C 199.14 (q), 151.42 (q), 140.32 (q), 135.25, 134.69, 134.09, 130.53, 128.78, 127.80, 117.23 (q), 116.02, 113.76, 111.68 and 44.97; *m/z* 237 (M$^+$, 100%), 236 (36), 167 (18), 132 (36), 105 (30), 91 (15) and 77 (45).

2-Allylamino-4′-methylbenzophenone **12** (from 2-amino-4′-methylbenzophenone[4]) (stirred for 72 h) (38%), b.p. 170–172 °C (0.6 Torr), m.p. 46–50 °C (Found: C, 81.1; H, 7.0; N, 5.85. $C_{17}H_{17}NO$ requires C, 81.3; H, 6.75; N, 5.6%); δ_H 8.62 (1 H, br s), 7.1–7.7 (6 H, m), 6.4–6.7 (2 H, m), 5.96 (1 H, m), 5.1–5.4 (2 H, m), 3.91 (2 H, m) and 2.41 (3 H, s); δ_C 192.81 (q), 151.36 (q),

Table 3 Observed and estimated ^{13}C NMR chemical shifts of some hydroxycarbazoles



	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-4b	C-8a	C-9a
Compound isolated from pyrolysate[a]	142.17	110.13	118.35	110.74	119.13	126.76	125.91	109.22	123.86	122.96	137.52	129.24
1-Hydroxycarbazole[b,c]	143.1	110.1	119.1	111.2	120.1	118.2	125.1	110.1	123.9	122.8	139.5	129.4
1-Hydroxy-6-methylcarbazole[d]	143.1	110.1	119.1	111.2	120.8	127.1	125.8	109.9	123.9	122.7	136.6	129.4

[a] [$^2H_6$]Acetone solution. [b] [$^2H_6$]DMSO solution. [c] Ref. 28. [d] Estimated from the data given for 1-hydroxycarbazole and the additivity effect of a methyl group in benzenoid systems.[26]

141.16 (q), 137.61 (q), 135.19, 134.51, 134.28, 129.20, 128.56, 117.63 (q), 116.10, 113.78, 111.69, 45.07 and 21.36; *m/z* 251 (M^+, 100%), 250 (35), 236 (14), 132 (14), 119 (9) and 91 (11).

2-*Allylamino*-4′-*methyldiphenyl sulphide* **14** (from 2-amino-4′-methyldiphenyl sulphide[8]) (30 h) (36%), b.p. 150–155 °C (0.2 Torr) (Found: C, 75.2; H, 6.5; N, 5.3. $C_{16}H_{17}NS$ requires C, 75.25; H, 6.7; N, 5.5%); δ_H 7.18–7.54 (2 H, m), 7.02 (4 H, s), 6.59–6.78 (2 H, m), 5.91 (1 H, m), 4.99–5.27 (2 H, m), 3.82 (2 H, m) and 2.28 (3 H, s) (NH signal not apparent); δ_C 148.98 (q), 137.19, 135.14 (q), 134.71, 133.04 (q), 130.90, 129.58, 126.71, 116.34, 115.71, 114.64 (q), 110.68, 45.75 and 20.75; *m/z* 255 (M^+, 100%), 226 (36), 199 (36), 136 (72), 130 (36), 109 (22), 91 (22), 77 (19) and 65 (21).

2-*Allylamino*-4′-*methyldiphenyl ether* **16** (from 2-amino-4′-methyldiphenyl ether[9]) (stirred for 18 h) (53%), b.p. 140–145 °C (0.4 Torr) (Found: C, 80.15; H, 7.1; N, 5.95. $C_{16}H_{17}NO$ requires C, 80.3; H, 7.15; N, 5.85%); δ_H 6.68–7.25 (8 H, m), 5.95 (1 H, m), 5.12–5.39 (2 H, m), 4.45 (1 H, br s), 3.85 (2 H, m) and 2.39 (3 H, s); δ_C 155.04 (q), 143.41 (q), 139.95 (q), 135.17, 132.04 (q), 129.98, 124.33, 118.51, 117.34, 116.57, 115.83, 111.70, 45.87 and 20.43; *m/z* 239 (M^+, 100%), 183 (29), 132 (16), 131 (33), 130 (23), 120 (35), 105 (25) and 91 (20).

2-*Benzylamino*-4′-*methyldiphenyl Ether* **17**.—A solution of 2-amino-4′-methyldiphenyl ether[9] (1.99 g, 10 mmol) and redistilled benzaldehyde (1.06 g, 10 mmol) in ethanol (20 cm^3) was kept for *ca.* 48 h in the presence of 4 Å molecular sieves. Removal of the solvent gave the crude *imine* **18** as an oil, which was freed from unchanged amine by careful bulb-to-bulb distillation at 175–180 °C (0.1 Torr) (1.73 g, 60%), δ_H 8.49 (1 H, s), 6.8–7.8 (13 H, m) and 2.30 (3 H, s); δ_C (non-quaternary signals only) 161.72, 131.22, 129.88, 128.77, 128.47, 126.34, 124.11, 121.31, 120.26, 117.91 and 20.50.

This material was not further purified, but was dissolved in methanol (20 cm^3), and reduced to the *N*-benzyl compound by treatment with solid sodium borohydride[10] (1.0 g, 25 mmol). After the addition of the reagent, the solution was heated under reflux for 15 min, the reaction mixture was added to water (30 cm^3), and the mixture was extracted with methylene dichloride (2 × 30 cm^3). The extracts were then dried (Na_2SO_4) and concentrated under reduced pressure. The N-*benzyl derivative* **17** (1.58 g, 92%) so obtained was an oil which soon crystallised, m.p. 61–62 °C (from hexane) (Found: C, 83.1; H, 6.65; N, 4.85. $C_{20}H_{19}NO$ requires C, 83.05; H, 6.55; N, 4.85%); δ_H 6.6–7.4 (13 H, m), 4.70 (1 H, br s), 4.41 (2 H, s) and 2.36 (3 H, s); δ_C 155.04 (q), 143.53 (q), 140.02 (q), 139.26 (q), 132.18 (q), 130.02, 128.44, 127.12, 126.98, 124.36, 118.44, 117.51, 116.71, 111.45, 47.64 and 20.50; *m/z* 289 (M^+, 18%), 199 (24), 183 (14), 91 (100), 65 (46) and 57 (17).

2-(4-*Methylphenylamino*)*benzyl Alcohol* **24** (cf. *Ref.* 31).—*N*-(4-Methylphenyl)anthranilic acid[32] (5.0 g, 22 mmol) was dissolved in dry tetrahydrofuran (THF) (7 cm^3) and the stirred mixture was cooled to 0 °C under dry nitrogen. A solution of diborane in THF (1 mol dm^{-3}; 75 cm^3) was added to the mixture, *via* a septum over a period of 15 min, and the resulting yellow solution was stirred at room temperature for 4.5 h. The mixture was then cooled to 0 °C and aq. sodium hydroxide (1 mol dm^{-3}; 6 cm^3) was slowly added to destroy excess of hydride. The reaction mixture was stirred overnight at room temperature to hydrolyse the amine–borane complex, then the pH of the resulting solution was adjusted to 11.0 by the addition of aq. sodium hydroxide. The aqueous phase was saturated with potassium carbonate, the THF phase was separated, and the aqueous phase was extracted with diethyl ether (4 × 50 cm^3). The combined organic layers were dried (Na_2SO_4), and the solvents were removed under reduced pressure. The crude product was purified by distillation to give 2-(4-*methylphenylamino*)*benzyl alcohol* **24** as a yellow oil (1.93 g, 41%), b.p. 130–132 °C (0.5 Torr) (Found: C, 78.65; H, 6.95; N, 6.55. $C_{14}H_{15}NO$ requires C, 78.85; H, 7.05; N, 6.55%); δ_H 6.74–7.35 (10 H, m), 4.71 (2 H, s) and 2.32 (3 H, s); δ_C 143.72 (q), 140.16 (q), 130.63 (q), 129.70, 129.36, 129.02, 127.75 (q), 119.69, 119.01, 116.10, 64.43 and 20.52; *m/z* 213 (M^+, 42%), 194 (62), 183 (46), 180 (46), 74 (58), 59 (100) and 45 (75).

Reaction of 2-(4-*Methylphenylamino*)*benzyl Alcohol with Oxalyl Chloride*.—Attempts were made to prepare the appropriate benzyl oxalate by the reaction of the benzyl alcohol with oxalyl chloride.[20] On removal of the solvent after work-up a thick, sticky oil was obtained, whose IR spectrum indicated that no carbonyl groups were present.

Pyrolysis Experiments.—NMR yields were obtained from small-scale pyrolyses, with cyclohexane (5 mm^3) as internal calibrant. Results are quoted as follows: quantity of substrate, inlet temperature, furnace temperature, pressure, pyrolysis time and products.

2-Allylaminodiphenylmethane **6** (0.158 g, 0.708 mmol), 110 °C, 750 °C, 1 × 10^{-3} Torr, 15 min: 2-aminodiphenylmethane (8%), *m/z* 183; acridine (11%), *m/z* 179; acridan (50%), *m/z* 181. On a preparative scale the amine (0.75 g, 3.36 mmol) was distilled at 1 × 10^{-3} Torr into a furnace at 775 °C over a period of 1 h. The crude pyrolysate (0.71 g) was recrystallised from ethanol to give a pure sample of acridan (0.329 g, 54%), m.p. 170–172 °C, mixed m.p. 169–172 °C (lit.,[33] 172–173 °C); δ_H 6.59–8.50 (8 H, m), 5.93 (1 H, br s) and 4.05 (2 H, s); δ_C 140.00 (q), 128.47, 126.87, 120.50, 119.89 (q), 113.29 and 31.24. The ^1H NMR and ^{13}C NMR spectra were identical with those of an authentic sample of acridan.[14]

2-Allylamino-4′-methyldiphenylmethane **8** (0.060 g, 0.253 mmol), 140 °C, 750 °C, 1 × 10^{-3} Torr, 40 min. The crude pyrolysate was dissolved in [^2H]chloroform and analysed, by NMR spectroscopy, for the presence of acridans. [Authentic 2-

methylacridan: δ_N −289.91; δ_H 7.06 (2 H, m), 6.78–6.91 (3 H, m), 6.60 (2 H, m), 5.88 (1 H, br s), 4.01 (2 H, s) and 2.26 (3 H, s); δ_C 140.29 (q), 137.59 (q), 129.71 (q), 128.98, 128.46, 127.33, 126.79, 120.19, 119.79 (q), 113.19, 21.23 and 20.45 (two signals coincidental at 113.19; two quarternary signals coincidental at δ_C 119.79).] The ^{13}C NMR spectrum of the crude pyrolysate showed two methylene peaks, at δ_C 31.23 and 30.83, and two methyl peaks, at δ_C 21.53 and 22.08, assigned to 2-methylacridan and 3-methylacridan, respectively. The ^1H NMR spectrum shows a methyl peak at 2.28, and methylene peak at 4.02, attributed to the methylacridan isomers. A ^{15}N NMR spectrum of the pyrolysate indicated two NH signals, at δ_N −290.08 and −288.95. From the NMR spectra obtained, the ratio of 2-methylacridan:3-methylacridan was found to be 2:1. The ^1H NMR spectrum obtained also indicated the presence of acridines in the pyrolysate, the aromatic signals being spread over the range 6.46–8.69 and a single peak being observed at δ_H 2.57. (An authentic sample of 2-methylacridine has a methyl resonance at δ_H 2.60.) The minor components of the pyrolysate were not identified.

2-Allylaminobenzophenone **10** (0.332 g, 1.401 mmol), 160 °C, 750 °C, 1 × 10^{-3} Torr, 20 min. The only product isolated was a yellow solid which formed at the exit point of the furnace. It had m.p. 348–350 °C (darkens > 300 °C). On a preparative scale the amine (1.362 g, 5.7 mmol) was distilled at 1 × 10^{-3} Torr into a furnace at 775 °C over a period of 50 min. The crude pyrolysate (0.877 g, 80%) was recrystallised from DMF to give acridone **25** (0.441 g), m.p. and mixed m.p. > 350 °C (decomposition > 340 °C) (lit.,[34] 354 °C) $\delta_H[(CD_3)_2SO]$ 8.18–8.31 (2 H, m), 7.14–7.84 (6 H, m) and 3.43 (1 H, br s); $\delta_C[(CD_3)_2SO]$ 176.80 (q), 140.91 (q), 133.44, 126.03, 121.00, 120.55 (q) and 177.33. The ^1H NMR and ^{13}C NMR spectra were identical with those of an authentic sample.

2-Allylamino-4′-methylbenzophenone **12** (0.124 g, 0.49 mmol), 120–150 °C, 750 °C, 3 × 10^{-3} Torr, 30 min. The pyrolysate was first washed with warm [^2H]chloroform, and the yellow crystalline residue was dissolved in $(CD_3)_2SO$. The chloroform fraction was weak and showed no clearly defined signals. The DMSO fraction was a clean 1:1 mixture of 2- and 3-methylacridone (*ca.* 50% total), $\delta_H[(CD_3)_2SO]$ 11.68 (1 H, s), 11.62 (1 H, s), 8.24 (2 H overlapping, d), 8.12 (1 H, d), 8.03 (1 H, s), 7.15–7.75 (9 H, m), 7.02 (1 H, d), 2.40 (3 H, s), and 2.37 (3 H, s); $\delta_C[(CD_3)_2SO]$ (DEPT 3π/4) 134.77, 133.07, 125.90, 124.96, 122.72, 120.73, 120.59, 117.15, 116.42, 21.43 and 20.47 (see also Discussion section).

2-Allylamino-4′-methyldiphenyl sulphide **14** (0.123 g, 0.482 mmol), 100 °C, 750 °C, 1 × 10^{-3} Torr, 15 min. *p*-Thiocresol, *m/z* 124; 3-methylphenothiazine (14%), *m/z* 213; 4-amino-8-methyldibenzothiophene (34%), *m/z* 213; 2-amino-4′-methyldiphenyl sulphide, *m/z* 215; and starting material (trace), *m/z* 255. No yields were calculated for the *p*-thiocresol or 2-amino-4′-methyldiphenyl sulphide but these were thought to be present in yields of *ca.* 3–5% from the GLC trace. There were two minor components of this pyrolysate, *m/z* 179 and *m/z* 182, which were not identified. On a preparative scale the amine (0.859 g, 3.37 mmol) was distilled at 10^{-3} Torr into a furnace at 750 °C over a period of 1.5 h. The entire pyrolysate was chromatographed on a column of alumina and eluted with diethyl ether (20%) in light petroleum (b.p. 40–60 °C). The following components were isolated: 3-methylphenothiazine (crude wt 0.236 g). This crude material was purified by sublimation to give 3-methylphenothiazine (0.078 g, 10%), probably contaminated with a small amount of the 2-methyl compound. The sublimed material had m.p. 150–153 °C (3-methylphenothiazine lit.,[35] 166–168 °C; 2-methylphenothiazine lit.,[6] 184–186 °C); $\delta_H[(CD_3)_2SO]$ 8.42 (1 H, br s), 6.51–7.12 (m) and 2.12 (3 H, m); $\delta_C[(CD_3)_2SO]$ 142.36 (q), 139.56 (q), 130.68, 127.94, 127.42, 126.45, 126.19, 121.42, 116.26 (q, 2Cs), 114.28 (2Cs) and 19.94. These ^1H NMR and ^{13}C NMR chemical shifts were identical with those of an authentic sample of 3-methylphenothiazine: $\delta_H[(CD_3)_2SO]$ 8.41 (1 H, br s), 6.52–7.08 (7 H, m) and 2.12 (3 H, s); $\delta_C[(CD_3)_2SO]$ 142.42 (q), 139.59 (q), 130.66 (q), 127.93, 127.42, 126.48, 126.21, 121.42, 116.38 (q, 2Cs), 114.30 and 19.96. The ^1H NMR spectrum of this fraction of the pyrolysate also had a peak at $\delta_H[(CD_3)_2SO]$ 2.15 which may be due to the presence of 2-methylphenothiazine. The ^{13}C NMR spectrum showed peaks corresponding to the calculated values for 2-methylphenothiazine as well as several impurity peaks. Comparison of the ^{13}C NMR spectrum with that of an authentic sample of 2,7-dimethylphenothiazine[25] also suggested the presence of some 2-methylphenothiazine (Table 1). 4-*Amino*-8-*methyldibenzothiophene* **29** (crude wt 0.217 g). The crude material was purifed by sublimation to give the *product* (0.110 g, 15%), m.p. 103–105 °C (Found: C, 73.05; H, 5.35; N, 6.65. $C_{13}H_{11}NS$ requires C, 73.2; H, 5.2; N, 6.55%); δ_H 7.92 (1 H, m), 7.74 (1 H, d), 7.62 (1 H, dd), 7.25–7.33 (2 H, m), 6.79 (1 H, dd), 3.88 (2 H, br s) and 2.52 (3 H, s); δ_C 140.86 (q), 136.53 (q, 2Cs), 135.64 (q), 134.09 (q), 128.02, 125.94 (q), 125.51, 122.44, 122.11, 112.34, 111.88 and 21.30.

2-Allylamino-4′-methyldiphenyl ether **16** (0.106 g, 0.443 mmol), 100 °C, 750 °C, 1 × 10^{-3} Torr, 15 min. Toluidine (trace), *m/z* 107; unidentified product (14%), *m/z* 197 (see below); and 2-(*p*-toluidino)phenol (20%), *m/z* 199. A sample of 2-(*p*-toluidino)phenol was isolated by preparative GLC (240 °C, SE 30), $\delta_H(CDCl_3$ + 1% dithionite in $D_2O)$ 6.66–7.17 (8 H, m) and 2.26 (3 H, s) [lit.,[36] δ_H 6.4–7.4 (8 H, m) and 2.25 (3 H, s)].

2-Benzylamino-4′-methyldiphenyl ether **17** (0.059 g, 0.20 mmol), 140 °C, 750 °C, 3 × 10^{-3} Torr, 20 min. The following products were identified by comparison of the ^1H NMR spectrum ([$^2H_6$]acetone) of the crude pyrolysate with those of authentic or isolated samples: bibenzyl (δ_H 2.92) (60%, based on available $PhCH_2^{\bullet}$); 2-(*p*-toluidino)phenol (δ_H 2.26) (23%); 1-hydroxy-6-methylcarbazole (δ_H 2.50) (36%).

On a preparative scale, the *N*-benzyl derivative was sublimed at 140–180 °C and 3 × 10^{-3} Torr during 90 min into the furnace at 750 °C. There was a considerable amount of tarry pyrolysate formed at the exit point of the furnace during the later stages of the pyrolysis, which was removed before work-up by a tissue soaked in methylene dichloride. The majority of the pyrolysate was then dissolved in warm chloroform: the insoluble solid residue was scraped out of the trap, and washed with a small amount of chloroform to give 1-hydroxy-6-methylcarbazole **35** (0.11 g, 28%), m.p. 192–194 °C (lit.,[29] 194–195 °C); δ_H([$^2H_6$]-acetone) 10.01 (1 H, br s), 8.58 (1 H, s), 7.86 (1 H, s), 7.59 (1 H, d), 7.46 (1 H, d), 7.22 (1 H, d), 6.99 (1 H, t), 6.88 (1 H, dd) and 2.49 (3 H, s) (the aromatics showed significant solvent shifts in $CDCl_3$); δ_C([$^2H_6$]acetone) 142.17 (q), 137.52 (q), 129.24 (q), 126.76 (q), 125.91, 123.86 (q), 122.96 (q), 119.13, 118.35, 110.74, 110.13, 109.22 and 19.81; *m/z* 197 (M^+, 100%), 196 (44) and 168 (6).

The original chloroform solution was extracted with dil. hydrochloric acid (1 mol dm^{-3}; 2 × 10 cm^3), and the combined aqueous layers were basified, and extracted with methylene dichloride (3 × 20 cm^3). The extracts were dried (Na_2SO_4) and concentrated to give a brown, semi-solid mass (0.03 g), which was mostly *p*-toluidine [δ_H 6.98 (2 H, d), 6.62 (2 H, d) and 2.26 (3 H, s)] (identified by spiking with an authentic sample).

The chloroform extracts (above) were then extracted with dil. aq. sodium hydroxide (1 mol dm^{-3}; 2 × 10 cm^3), and the combined aqueous layers were acidified and extracted with methylene dichloride (2 × 10 cm^3). The extracts were dried (Na_2SO_4) and concentrated to give a brown oil (0.11 g), which was a 3:1 mixture of *p*-toluidinophenol (20%) (δ_H 2.36) and the above hydroxycarbazole (total yield 35%) (δ_H 2.60).

The chloroform extracts (above) were dried (Na_2SO_4) and

concentrated to yield a neutral fraction (0.21 g) which was predominantly bibenzyl [δ_H 7.35–7.55 (10 H, m) and 3.14 (4 H, s)].

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