Gas-phase cyclisation reactions of 1-(2-arylaminophenyl)alkaniminyl radicals

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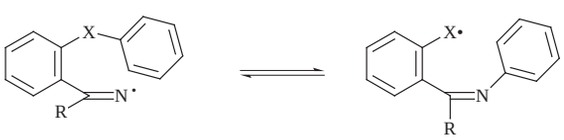
Flash vacuum pyrolysis (FVP) of the oxime ethers 9–11 at 650 °C (10^{-2}–10^{-3} Torr) gives products such as the nitrile 17, carbazoles 19 and 20 and acridines 18 and 21 derived from the corresponding iminyl radicals 13–15. The mechanism proposed for the formation of the acridines involves a key hydrogen abstraction by the iminyl of the adjacent N–*H* atom. When this route is blocked by an *N*-methyl group, as in 12, alternative cyclisations ensue, yielding the dihydroquinazoline 26 (*via* another hydrogen abstraction process) and the benzimidazole 25 (*via* an iminyl–imidoyl interconversion).

In an accompanying paper,[1] we have reported the reactions of 1-(2-aryloxyphenyl)- and 1-(2-arylaminophenyl)-alkaniminyl radicals generated in solution. Our corresponding work on 1-(2-aryloxyphenyl)alkaniminyls **1** generated in the gas phase by flash vacuum pyrolysis (FVP) has led to the observation of interconversion processes relating these iminyls and 2-(aryliminomethyl)phenoxyl radicals **2** (Scheme 1, X = O).[2]



1 (X = O)
3 (X = NR)

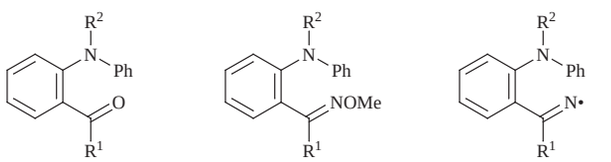
2 (X = O)
4 (X = NR)

Scheme 1

Here we discuss the properties of the 1-(2-arylaminophenyl)-alkaniminyls **3** in the gas phase which surprisingly show quite different cyclisation behaviour; in particular we have no evidence for the interconversion of these species and 2-(aryliminomethyl)aminyl radicals **4** (Scheme 1, X = NR).

As before,[2,3] the iminyls were generated by FVP of oxime *O*-methyl ethers and we chose to study three series of radicals, bearing respectively a hydrogen atom, a methyl group and a phenyl group on the iminyl carbon atom.[1,2] The precursor aldehydes **5**[4] and **8** were obtained in four-step McFadyen–Stevens sequences starting from *N*-phenylanthranilic acid and *N*-methyl-*N*-phenylanthranilic acid respectively, whereas the ketones **6** and **7** were made by standard methods involving copper-catalysed *N*-arylation of 2-aminoacetophenone[5] and 2-aminobenzophenone[6] respectively with iodobenzene. The oxime ethers **9**–**12** were made in 70–92% yield by condensation of the carbonyl compounds **5**–**8** with *O*-methylhydroxylamine hydrochloride in the presence of pyridine.

The mass spectra of all the oxime ethers **9**–**12** show loss of *m*/*z* 31 (MeO) from their molecular ions. The ketone derivatives **10** and **11** both show significant peaks at *m*/*z* 194, corresponding to subsequent loss of the substituent attached to the oxime carbon atom, whereas the aldehyde derivatives **9** and **12** display a loss of *m*/*z* 15 as the next breakdown. Whereas this is probably due to cleavage of the *N*-methyl group in **12** (giving rise to the base peak at *m*/*z* 194) this is not possible for **9** and the peak is most likely due to loss of an NH unit (*m*/*z* 180, 30%). The



5 $R^1 = R^2 = H$
6 $R^1 = Me$, $R^2 = H$
7 $R^1 = Ph$, $R^2 = H$
8 $R^1 = H$, $R^2 = Me$

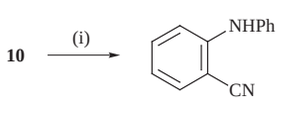
9 $R^1 = R^2 = H$
10 $R^1 = Me$, $R^2 = H$
11 $R^1 = Ph$, $R^2 = H$
12 $R^1 = H$, $R^2 = Me$

13 $R^1 = R^2 = H$
14 $R^1 = Me$, $R^2 = H$
15 $R^1 = Ph$, $R^2 = H$
16 $R^1 = H$, $R^2 = Me$

oxime ethers **9**–**12** also show common peaks at *m*/*z* 167, which may be due to a carbazole-like species, after cleavage of the entire oxime unit and cyclisation. Some of these processes are reflected in the thermal behaviour of the compounds (see below).

Under our standard conditions for oxime ether pyrolysis,[2,3] [650 °C (0.001–0.01 Torr)] the substrates **9**–**12** were transformed completely into products, presumably *via* the iminyls **13**–**16** respectively. Mixtures of products were generally obtained, and these were separated by chromatography on silica.

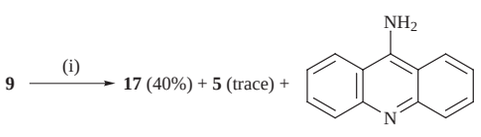
The acetophenone derivative **10** showed the simplest pyrolysate, being transformed exclusively into 2-(*N*-phenylamino)-benzonitrile **17** (92%) (Scheme 2). FVP of the oxime ether



10 → (i) → **17** (92%)

Scheme 2 *Reagents and conditions*: (i) 650 °C, 0.005 Torr

9 gave three products which were readily identified as 9-aminoacridine **18** (40%), 2-(*N*-phenylamino)benzonitrile **17** (40%) and a trace of 2-(*N*-phenylamino)benzaldehyde **5** (Scheme 3).



9 → (i) → **17** (40%) + **5** (trace) + **18** (40%)

Scheme 3 *Reagents and conditions*: (i) 650 °C, 0.003 Torr

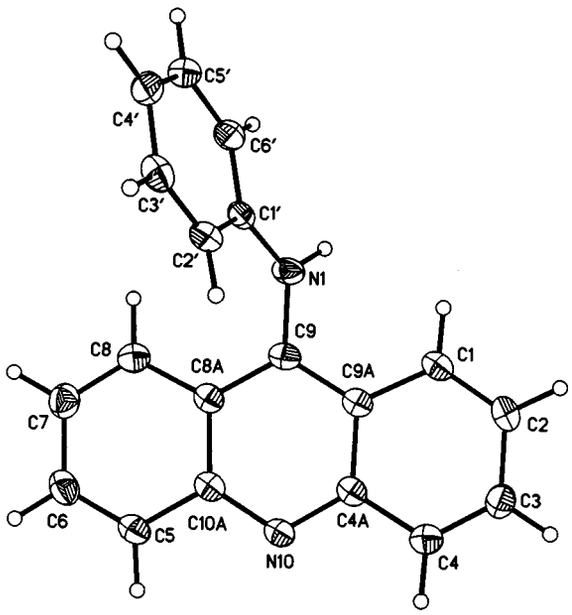
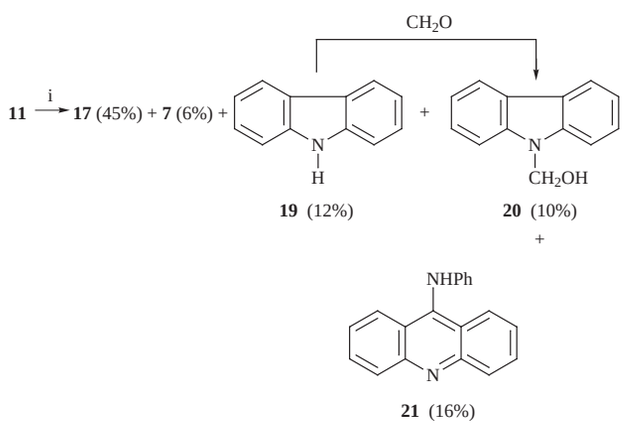


Fig. 1 A view of the acridine **21** showing the crystallographic numbering scheme: displacement ellipsoids enclose 50% probability surfaces

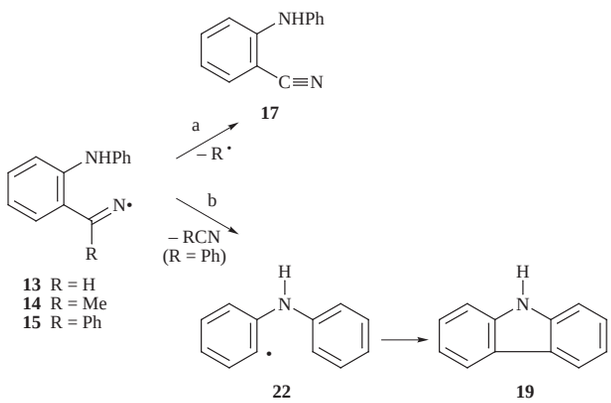
Five products were obtained from the pyrolysis of the benzophenone derivative **11**, *viz* the nitrile **17** (45%), the benzophenone **7** (6%), carbazole **19** (12%) and its 9-methanol derivative **20** (10%), and 9-phenylaminoacridine **21** (16%) (Scheme 4). The initial identification of the nitrile **17**, the acridine **18** and



Scheme 4 *Reagents and conditions*: (i) 650 °C, 0.005 Torr

the carbazoles **19** and **20** was made by mass spectrometry followed by comparison of their NMR spectra and other physical properties with those quoted in the literature (see Experimental section). The carbazol-9-ylmethanol **20** was unexpected, and may be formed by secondary reaction during work-up of the carbazole **19** with formaldehyde (Scheme 4).[7] Although we have not previously observed products derived from formaldehyde in oxime ether pyrolyses, this may be formed from the methoxyl radicals co-produced with the iminyls by homolysis of the N–O bond of the oxime ethers. The NMR spectra of the fraction which ultimately proved to be 9-phenylaminoacridine **21** showed temperature dependent broad signals owing to unidentified exchange processes which meant that it could not be identified spectroscopically. This product was therefore characterised unambiguously by X-ray crystallography (Fig. 1) (see below).

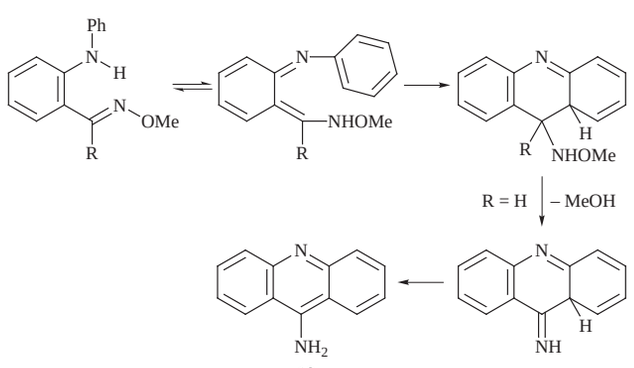
The carbonyl compounds **5** and **7** may be formed either by adventitious hydrolysis of the oxime ethers in the FVP inlet system during sublimation, or *via* (intermolecular) hydrogen capture by the iminyl and hydrolysis of the resulting imine during chromatography (*cf*. ref. 1). Otherwise the mechanism of formation of most of the products of these pyrolyses can be deduced on the basis of previous work with iminyls. Thus the nitrile **17**, which is common to all three precursors **9**, **10** and **11**, is formed by β-cleavage of a hydrogen atom, a methyl group and a phenyl group respectively from the iminyls **13**–**15** (Scheme 5, route a). Since such β-cleavage of a methyl group is



Scheme 5

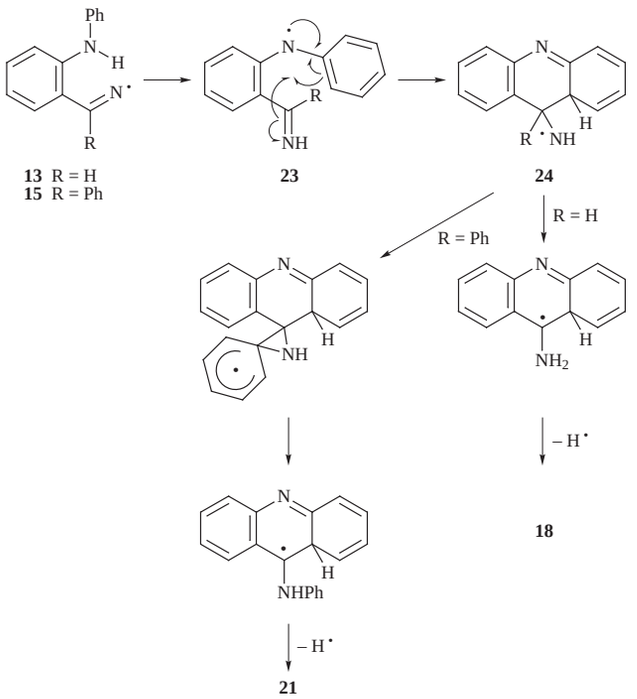
known to be facile relative to that of hydrogen atoms or aryl groups,[2,8] it is not surprising that this mechanism dominates the behaviour of the acetophenone derivative **10**. The alternative cleavage of an RCN group (Scheme 5, route b), which leads ultimately to carbazole **19** *via* cyclisation of the resulting aryl radical **22**,[9] is found only from the phenyl substituted iminyl radical **15** where β-cleavage by the two routes a and b leads to different aryl radicals. This route does not compete to any significant extent in the pyrolyses of **9** or **10**, which is in general agreement with the results from correspondingly substituted 1-(2-aryloxyphenyl)alkaniminyls **1**.[2]

The source(s) of the acridines **18** and **21** are of particular interest, since acridines (though not the 9-amino derivatives) are significant products from the generation of the iminyls **13**–**15** in solution[1] and no corresponding products are obtained from the related 1-(*o*-phenoxyphenyl)alkaniminyls.[1,2] It is clear that the N–*H* atom is transferred at some stage of the process, and we initially believed that **18** might be formed by a non-radical mechanism involving a 1,5-hydrogen shift, electrocyclisation and elimination (Scheme 6), similar in the early stages



Scheme 6

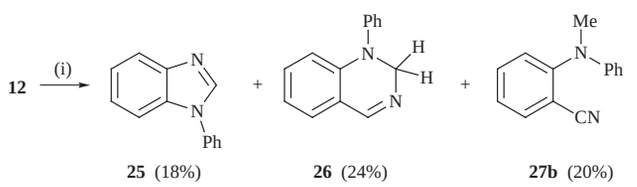
to the formation of acridones from *N*-phenylanthranilic acid esters.[10] However, this route cannot readily account for the production of **21** and we now believe that the mechanism of Scheme 7 is most likely. In this case, the iminyl is involved in the hydrogen transfer and the aminyl **23** thus obtained initiates the cyclisation. Further evidence for intramolecular hydrogen abstraction by iminyls is presented below, and the corresponding intermolecular process has been observed under solution conditions.[1] The primary aminyl **24** so obtained can achieve greater stability *via* a 1,2- (or possibly a 1,3-) shift of a hydrogen



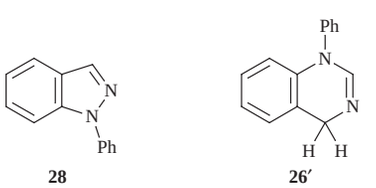
Scheme 7

atom (which may be intermolecular) giving the immediate precursor to **18**, or a 1,2-shift of the phenyl group (*via* a neophyl-type rearrangement) giving the immediate precursor to **21**.

It is clear that *N*-methylation would block the formation of acridines by these mechanisms and so the precursor **12** was synthesised in the hope that the pyrolysate mixture might be simplified. In the event, although no acridines were obtained, the availability of hydrogen atoms in the methyl group for hydrogen transfer caused further complications and the benzimidazole **25** (*m*/*z* 194) (18%) and the dihydroquinazoline **26** (*m*/*z* 208) (24%) were obtained along with the expected nitrile **27b** (20%) (Scheme 8). The component with *m*/*z* 194 was



Scheme 8 *Reagents and conditions*: (i) 650 °C, 0.005 Torr



initially thought to be the indazole **28**, but this structure was readily excluded on the basis of its NMR spectra.[11] In particular the ^{13}C NMR spectrum of 1-phenylindazole shows no signals at δ_C >138 whereas the observed peaks at δ_C 143.70 (quaternary) and 141.96 are in excellent agreement with those known for **25** (δ_C 143.7 and 142.3 respectively[11]). Product **27b** was also easily identified (see Experimental section), but the structure of the unusual quinazoline **26** was deduced from the following NMR experiments. The ^1H NMR spectrum (360 MHz) showed a slightly broadened imine triplet at δ_H 8.18 which was shown by decoupling to interact with a methylene doublet at δ_H 5.26 (*J* 1.9 Hz). The size of the coupling constant supports the idea that these protons are in the same ring, but

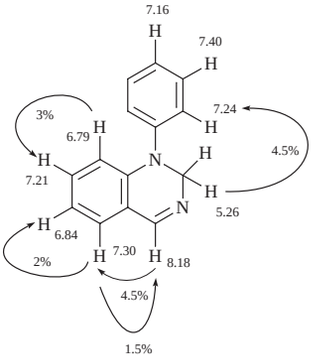
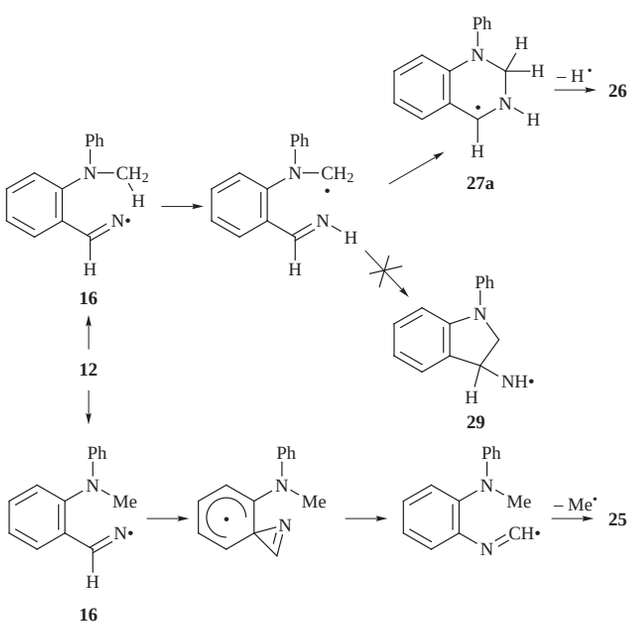


Fig. 2 ^1H NMR data for the 1,2-dihydroquinazoline **26**

suggests that they are attached to non-adjacent carbon atoms. The characteristic triplet (2H), doublet (2H), triplet (1H) pattern due to the *meta*, *ortho* and *para* protons respectively of a phenyl ring could also be discerned at δ_H 7.40, 7.24 and 7.16. The remaining signals were an equally characteristic doublet, triplet, triplet, doublet pattern at δ_H 7.30, 7.21, 6.84 and 6.79 due to an *ortho*-disubstituted (fused) benzene ring. NOE experiments (Fig. 2) related the imine proton to the doublet at δ_H 7.30, which allowed the assignments of the other protons in the fused ring as shown. Another key NOE experiment related the methylene protons to the *ortho* protons of the phenyl group (Fig. 2). The structure **26** is consistent with these observations and in particular the tautomer **26′** can be unambiguously excluded.

The formation of the dihydroquinazoline **26** clearly requires functionalisation of the *N*-methyl group of the substrate **12**, and this is most likely achieved by hydrogen atom abstraction by the iminyl (Scheme 9). A 6-*endo*-*trig* cyclisation onto the



Scheme 9

aldimine function generates the quinazoline ring system which leads to **26** by loss of a hydrogen atom. The driving force for the 6-*endo*-*trig* mode of cyclisation is presumably the formation of the stabilised benzyl radical **27a** rather than the primary aminyl **29** obtained by the alternative 5-*exo*-*trig* ring closure.

The source of the benzimidazole **25** is also of interest; in this case a skeletal rearrangement and loss of a C_1 unit has taken place. A number of mechanisms can be drawn for this transformation, of which the most likely is an iminyl to imidoyl radical interconversion followed by cyclisation and ejection of the *N*-methyl group (Scheme 9). It is perhaps surprising that

such neophyl-type rearrangements of iminyls to imidoyls has not been previously observed, and experiments are in progress to probe the feasibility of this step in more detail. At this stage, we cannot completely exclude the possibility that the primary product of the reaction is the indazole **28** which rearranges under the reaction conditions to the benzimidazole **25**; conversion of certain indazoles to benzimidazole derivatives is known under photochemical conditions.[12] However, FVP of 1-adamantylindazole under comparable conditions to ours rearranges only to its 2-isomer and to 2-(*N*-adamantylamino)-benzonitrile, with no benzimidazoles being formed.[13] In our case, the corresponding product [2-(*N*-phenylamino)benzonitrile **17**] was not found in the pyrolysate from **12** and so we believe that the indazole **28** is probably not involved in our transformations. A third possible mechanism involving initial loss of the *N*-methyl group is also unlikely because such homolysis is only partially complete even at 900 °C in diarylamine derivatives using our apparatus, compared with the furnace temperature of 650 °C used in the present study.[9] In any event, these three possible mechanisms differ only in the timing of the loss of the *N*-methyl group.

Finally, the crystal structure of the 9-(phenylamino)acridine **21** will be briefly discussed (Fig. 1). Previous crystallographic studies of 9-(arylamino)acridines have focused on derivatives with substituted *N*-aryl groups which have anticancer properties[14,15] and our compound is therefore the parent of this important class of materials. The acridine moiety of **21** is approximately planar, with the maximum deviation [at C(7)] being 0.145 Å. However, a minor 'butterfly' distortion about the C(9)–N(10) axis is observed, similar to that which has been previously noted for other 9-(arylamino)acridines.[15] The plane of the phenyl group forms an angle of 67.4° with the best plane of the acridine. The acridine ring is highly symmetric about a plane through C(9)–N(10), but the bonds linking C(1)–C(2) and C(3)–C(4) [and C(5)–C(6) and C(7)–C(8)] are, at a mean of 1.359(2) Å, significantly shorter than the other bonds in the fused benzene rings [mean 1.426(2) Å]. This feature is also common to the other acridines.[14,15] Bond angles in **21** are all close to 120°, with the largest deviations (up to +3.5° and −2.5°) being associated with angles in the central ring. The intermolecular packing of **21** involves the formation of chains *via* hydrogen bonding between N(10) and H(1′) ($\frac{1}{2} + x$, $-\frac{1}{2} - y$, z) [N(10)–N(1′) 2.975(2) Å].

In conclusion, this work has shown that in the gas phase, the cyclisation reactions of 1-(2-arylaminophenyl)alkaniminyl radicals are controlled by hydrogen transfer processes from the NH (if present) to give acridines, or from an *N*-alkyl group (if present) to give benzimidazole or quinazoline ring systems. Although the results have raised interesting questions—such as the possibility of iminyl–imidoyl interconversions—none of the cyclisation routes are particularly efficient and no evidence for the anticipated 1-(2-arylaminophenyl)alkaniminyl–2-(aryliminomethyl)aminyl radical interconversion was obtained though this is known to take place in solution.[1] Good evidence for the analogous gas-phase rearrangement in the 'oxygen' series is presented in the accompanying paper.[2]

Experimental

^{1}H and ^{13}C NMR species are recorded at 250 (or 200) and 63 (or 50) MHz respectively for solutions in [^{2}H]chloroform unless otherwise stated. Coupling constants are quoted in Hz.

2-(*N*-Phenylamino)benzaldehyde *O*-methyloxime 9

A solution of 2-(*N*-phenylamino)benzaldehyde **5**[4] (0.99 g, 5 mmol) and *O*-methylhydroxylamine hydrochloride (0.83 g, 10 mmol) was heated under reflux in ethanol (25 cm^3) in the presence of pyridine (0.79 g, 10 mmol) for 1 h. The solvent was removed under reduced pressure and the residue was partitioned between ether and dilute hydrochloric acid. The organic fractions were dried ($MgSO_4$) and the solvent was removed to give the *oxime* (1.04 g, 92%), mp 75–77 °C (from isopropyl alcohol) (Found: C, 74.25; H, 6.2; N, 12.45. $C_{14}H_{14}N_2O$ requires C, 74.35; H, 6.2; N, 12.4%); δ_H 9.02 (1H, br s), 8.22 (1H, s), 7.40–7.03 (8H, m), 6.79 (1H, m) and 3.98 (3H, s); δ_C 151.83, 143.71 (q), 141.12 (q), 132.73, 130.14, 129.24, 122.93, 121.60, 117.74, 115.61 (q), 113.20 and 62.05; *m*/*z* 226 (M^+, 82%), 195 (100), 180 (30), 168 (18) and 167 (46).

2′-(*N*-Phenylamino)acetophenone *O*-methyloxime 10

A solution of 2′-(*N*-phenylamino)acetophenone **6**[5] (1.06 g, 5 mmol) and *O*-methylhydroxylamine hydrochloride (0.83 g, 10 mmol) was heated under reflux in ethanol (25 cm^3) in the presence of pyridine (0.79 g, 10 mmol) for 6 h. A similar work-up to that described for **9** gave the *oxime* **10** (0.98 g, 82%), mp 85–86 °C (from methanol) (Found: C, 74.8; H, 6.9; N, 11.5. $C_{15}H_{16}N_2O$ requires C, 75.0; H, 6.65; N, 11.65%); δ_H 9.48 (1H, br s), 7.46–6.84 (9H, m), 4.02 (3H, s) and 2.31 (3H, s); δ_C 156.61 (q), 142.35 (q), 142.10 (q), 129.05, 129.18, 121.78, 121.18, 120.01, 120.67 (q), 118.38, 115.48, 61.92 and 13.53; *m*/*z* 240 (M^+, 100%), 209 (87), 194 (16), 182 (8) and 167 (46).

2-(*N*-Phenylamino)benzophenone *O*-methyloxime 11

A solution of 2-(*N*-phenylamino)benzophenone **7**[6] (1.6 g, 5.8 mmol) and *O*-methylhydroxylamine hydrochloride (1.08 g, 5.8 mmol) was heated under reflux in a mixture of ethanol (30 cm^3) and pyridine (15 cm^3) for 2 days. A similar work-up to those described above gave the *oxime* **11** (1.61 g, 92%), as a yellow oil which was a mixture of *Z* and *E* isomers (Found: M^+, 302.1434. $C_{20}H_{18}N_2O$ requires *M*, 302.1419); δ_H 9.80 (1H, br s), 7.82–6.74 (28H, m), 6.08 (1H, br s), 4.20 (3H, s) and 4.09 (3H, s) (^{13}C NMR spectrum not quoted because of its complexity); *m*/*z* 302 (M^+, 93%), 271 (52), 269 (100), 195 (48), 194 (40), 167 (54) and 77 (40).

2-(*N*-Methyl-*N*-phenylamino)benzaldehyde 8

This compound was made by McFadyen–Stevens degradation of *N*-methyl-*N*-phenylanthranilic acid[16] without full characterisation of the intermediates involved. Thus, *N*-methylation of *N*-phenylanthranilic acid was achieved by heating overnight with an excess of iodomethane in dilute sodium hydroxide solution.[16] The resulting mixture of *N*-methyl-*N*-phenylanthranilic acid (*ca*. 65%) and starting material (both partially esterified) was hydrolysed to the corresponding acids under strongly basic conditions, and these precipitated on acidification. Without purification, this mixture (18.69 g, *ca*. 0.088 mol) was esterified overnight using iodomethane (14.2 g, 0.1 mol) in dimethylformamide (250 cm^3) in the presence of potassium carbonate (12.2 g, 0.088 mol). After the usual work-up,[2] the resulting mixture of esters was separated using column chromatography on silica [using hexane and ethyl acetate (2.5%) as eluents] to give methyl *N*-methyl-*N*-phenylanthranilate (8.5 g, 40%) as a yellow oil, δ_H 7.85 (1H, m), 7.55 (1H, m), 7.34–7.18 (4H, m), 6.82–6.68 (3H, m), 3.62 (3H, s) and 3.33 (3H, s); δ_C 167.04 (q), 148.84 (q), 147.73 (q), 132.91, 131.03, 128.84 (q), 128.64, 128.52, 124.84, 117.63, 113.87, 51.62 and 40.00; *m*/*z* 241 (M^+, 100%), 210 (27), 208 (30), 195 (10), 182 (23), 180 (30), 167 (23) and 106 (13).

This ester (7.5 g, 0.031 mol) was then heated under reflux with hydrazine hydrate (2.35 g, 0.047 mol) for 10 h, cooled and washed twice with water. The thick oily residue soon solidified and was recrystallised from ethanol to give the hydrazide (6.90 g, 92%), mp 88–90 °C, δ_H 9.35 (1H, br s), 8.09 (1H, m), 7.47–7.04 (5H, m), 6.86–6.57 (3H, m), 4.18 (2H, br s) and 3.11 (3H, s); δ_C 166.46 (q), 148.66 (q), 147.80 (q), 132.48, 130.72 (q), 128.69, 127.35, 126.11, 119.74, 115.83, 113.78 and 40.44; *m*/*z* 241 (M^+, 49%), 210 (100), 195 (10) and 180 (10).

The hydrazide (5.68 g, 0.024 mol) was tosylated by slow addition of toluene-*p*-sulfonyl chloride (4.49 g, 0.024 mol) to a solution in dry pyridine (10 cm^3). The reaction temperature

was kept below 60 °C. The solution was left to stand at room temperature for 2 h, and then poured into a mixture of ice and dilute hydrochloric acid to give the toluene-*p*-sulfonohydrazide as a thick oil which soon solidified. It was filtered, washed with water and recrystallised from ethanol to give yellow crystals (7.56 g, 80%), mp 148–150 °C, δ_H 10.56 (1H, br s), 7.95 (1H, dd, ^3J 7.8, ^4J 1.7), 7.70–7.60 (2H, d, ^3J 8.3), 7.49 (1H, td, ^3J 7.5, ^4J 1.7), 7.35–7.05 (7H, m), 6.97 (1H, m), 6.80–6.70 (2H, d, ^3J 8.3), 3.19 (3H, s) and 2.36 (3H, s); δ_C 163.76 (q), 148.92 (q), 148.86 (q), 144.42 (q), 133.84, 133.39 (q), 131.29, 129.36, 129.08, 128.24, 127.69, 127.32 (q), 126.67, 121.05, 117.01, 41.28 and 21.51; *m*/*z* 395 (M^+, 12%), 210 (100), 195 (17), 180 (9), 167 (10), 91 (15) and 77 (10).

A solution of the toluene-*p*-sulfonohydrazide (6.45 g, 0.016 mol) in ethylene glycol (30 cm^3) was degraded to the aldehyde by addition of anhydrous sodium carbonate (4.02 g, 0.038 mol) at 160 °C as fast as foaming allowed, according to the general method of McFadyen and Stevens (*cf*. ref. 4). The reaction mixture was maintained at that temperature for 4 min, cooled and diluted with water to give a brown solid. Careful recrystallisation from methanol gave 2-(N-*methyl*-N-*phenylamino*)*benzaldehyde* **8** as a soft yellow solid (2.36 g, 70%), mp 48–50 °C, δ_H 10.15 (1H, s), 7.95 (1H, m), 7.64 (1H, m), 7.37–7.16 (4H, m), 6.86–6.72 (3H, m) and 3.37 (3H, s); δ_C 191.19, 151.80 (q), 149.84 (q), 135.67, 132.46 (q), 129.07, 128.70, 127.50, 125.80, 118.94, 114.96 and 41.33; *m*/*z* 211 (M^+, 100%), 195 (11), 194 (45), 182 (68), 180 (20), 168 (93), 167 (83), 106 (24), 91 (30) and 77 (42). This aldehyde was characterised as its oxime ether (see below).

2-(*N*-Methyl-*N*-phenylamino)benzaldehyde *O*-methyloxime 12

A solution of 2-(*N*-methyl-*N*-phenylamino)benzaldehyde **8** (1.88 g, 8.9 mmol) and *O*-methylhydroxylamine hydrochloride (1.49 g, 18 mmol) in ethanol (40 cm^3) containing pyridine (3 cm^3) was heated under reflux for 1 h. After the standard work-up, the *oxime* (1.88 g, 88%), mp 102–103 °C (from isopropyl alcohol) was obtained (Found: C, 74.7; H, 7.0; N, 11.55. $C_{15}H_{16}N_2O$ requires C, 75.0; H, 6.65; N, 11.65%); δ_H 8.13 (1H, s), 7.96 (1H, dd, ^3J 7.0 and ^4J 1.9), 7.45–7.13 (5H, m), 6.75 (1H, apparent t, ^3J 7.0), 6.59 (2H, m), 3.93 (3H, s) and 3.21 (3H, s); δ_C 149.28 (q), 147.51 (q), 145.84, 131.36, 130.40, 128.89, 128.22 (q), 126.73, 126.48, 117.76, 113.70, 61.85 and 40.17; *m*/*z* 240 (M^+, 27%), 209 (91), 194 (100), 180 (69), 167 (14), 131 (11), 91 (13) and 77 (26).

Flash vacuum pyrolysis experiments

The substrate was sublimed at 0.01–0.001 Torr through a silica tube which was maintained at the appropriate temperature by an electrically heated tube furnace. Products were collected in a U-tube trap cooled by liquid nitrogen located at the exit point of the furnace and thereafter were usually separated by dry-flash chromatography on silica. Results are presented in the form quantity of substrate, inlet temperature, furnace temperature, pressure, pyrolysis time and products.

Pyrolysis of 2-(*N*-phenylamino)benzaldehyde *O*-methyloxime 9. (0.37 g, 1.6 mmol) 60–90 °C, 650 °C, 3×10^{-3} Torr, 2 h: a yellow solid was formed at the exit-point of the furnace which could be dissolved in acetone. Removal of the solvent gave 9-aminoacridine **18** (0.13 g, 40%), mp 233–234 °C (lit.,[17] 233 °C), δ_H([$^2H_6$]DMSO) 8.38 (2H, dd), 7.81 (2H, dd), 7.63 (2H, ddd), 7.29 (2H, ddd) and 4.42 (2H, br s); δ_C([$^2H_6$]DMSO) 150.27 (q), 148.79 (q), 129.98, 128.61, 123.41, 121.61 and 112.98 (q), (spectrum consistent with literature data[18]); *m*/*z* 194 (M^+, 100%), 193 (15), 167 (6), 166 (9), 97 (7), 84 (7) and 66 (15); chromatography of the remainder of the pyrolysate gave a trace of 2-(*N*-phenylamino)benzaldehyde **5** (0.019 g, 6%) and 2-(*N*-phenylamino)benzonitrile **17** (0.12 g, 40%), mp 55–57 °C (lit.,[19] 50–52 °C), δ_H 7.50 (1H, m), 7.39–7.20 (3H, m), 7.17–7.09 (4H, m), 6.83 (1H, m) and 6.42 (1H, br s); δ_C 147.20 (q), 139.80 (q), 133.76, 132.93, 129.46, 124.02, 121.54, 119.09, 117.49 (q), 114.04 and 98.33 (q); *m*/*z* 194 (M^+, 100%), 193 (28), 168 (10), 167 (15), 166 (11) and 77 (18).

Pyrolysis of 2′-(*N*-phenylamino)acetophenone *O*-methyloxime 10. (0.42 g, 1.8 mmol) 90 °C, 650 °C, 5×10^{-3} Torr, 2 h: the sole significant product isolated after chromatography was 2-(*N*-phenylamino)benzonitrile **17** (0.32 g, 92%) (spectra as above).

Pyrolysis of 2-(*N*-phenylamino)benzophenone *O*-methyloxime 11. (0.64 g, 2.1 mmol) 90–120 °C, 650 °C, 5×10^{-3} Torr, 3 h: a chloroform-insoluble fraction was identified as carbazole **19** (0.05 g, 12%), mp 236–238 °C (lit.,[20] 245 °C), spectra identical with those in the literature.[21] The chloroform-soluble fraction was separated by chromatography (eluted with hexane–ethyl acetate) to give 2-(*N*-phenylamino)benzonitrile **17** (0.18 g, 45%), (spectra as above): carbazol-9-ylmethanol **20** (0.04 g, 10%), mp 130–132 °C (lit.,[7] 128–139 °C), δ_H 8.11–8.05 (2H, m), 7.55–7.20 (6H, m), 5.80 (2H, s) and 2.70 (1H, br s); δ_C 139.55 (q), 125.91, 120.47 (q), 120.34, 119.97, 108.73 and 66.40; *m*/*z* 197 (M^+, 32%), 180 (6), 168 (14), 167 (100), 166 (23) and 139 (13); 9-phenylaminoacridine **21** (0.09 g, 16%), crude mp 198–200 °C (lit.,[22] 224 °C), *m*/*z* 270 (M^+, 100%), 269 (81), 268 (42) and 135 (16). This compound showed broad peaks in its NMR spectra due to exchange effects at room temperature, and so it was characterised by X-ray crystallography (see below and Discussion section). A small quantity of 2-(*N*-phenylamino)-benzophenone **7** (6%) was also recovered.

Pyrolysis of 2-(*N*-methyl-*N*-phenylamino)benzaldehyde *O*-methyloxime 12. (0.60 g, 2.5 mmol) 90–120 °C, 650 °C, 5×10^{-3} Torr, 2.5 h: 2-(N-*methyl*-N-*phenylamino*)*benzonitrile* **27b** (0.10 g, 20%) (Found: M^+, 208.0999. $C_{14}H_{12}N_2$ requires *M*, 208.1000); δ_H 7.56 (1H, m), 7.43–7.11 (4H, m), 6.98–6.80 (3H, m), 6.67 (1H, m) and 3.39 (3H, s); δ_C(CH and CH_3 signals only) 134.41, 133.73, 129.08, 125.51, 123.77, 120.90, 117.86 and 40.67; *m*/*z* 208 (M^+, 100%), 207 (51), 192 (13), 180 (10), 167 (8), 131 (25), 129 (14), 104 (12), 91 (19) and 77 (25); 1-phenylbenzimidazole **25** (0.09 g, 18%); δ_H 8.06 (1H, s), 7.79–7.90 (2H, m), 7.55–7.35 (5H, m) and 7.32–7.20 (2H, m); δ_C 143.70 (q), 141.96, 135.98 (q), 133.33 (q), 129.72, 127.69, 123.67, 123.38, 122.47, 120.23 and 110.16 (spectrum consistent with literature data[11]); *m*/*z* 194 (M^+, 100%), 193 (10), 77 (11) and 51 (13); 1-*phenyl*-1,2-*dihydroquinazoline* **26** (0.12 g, 24%) (Found: M^+, 208.1008. $C_{14}H_{12}N_2$ requires *M*, 208.1000); δ_H 8.18 (1H, m), 7.46–7.32 (3H, m), 7.26–7.11 (4H, m), 6.85–6.78 (2H, m) and 5.26 (2H, d) (see also Fig. 1); δ_C 158.63, 144.60 (q), 143.62, 132.43, 129.16, 127.74, 124.23, 123.04, 119.70 (q), 119.23, 114.49 (q) and 61.81; *m*/*z* 208 (M^+, 55%), 207 (100), 195 (14), 180 (27), 168 (14), 167 (12) and 77 (26).

X-Ray crystallography

Crystal data. $C_{19}H_{14}N_2$, $M = 270.32$, monoclinic, $a = 12.2580(14)$, $b = 8.6809(6)$, $c = 13.0712(10)$ Å, $\beta = 92.051(10)°$, $U = 1390$ Å^3 [from 2θ values of 45 reflections ($30 < 2\theta < 39°$) measured at $\pm\omega$], $T = 150$ K, space group $P2_1/a$, graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\,73$ Å, $Z = 4$, $D_c = 1.292$ Mg m^{-3}, $F(000) = 568$, yellow block with dimensions $0.70 \times 0.51 \times 0.31$ mm^3. Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device, ω–θ scans, data collection range $5 < 2\theta < 50°$, $-14 < h < 14$, $0 < k < 10$, $0 < l < 15$. Three standard reflections showed no significant intensity variation; 2457 unique data.

Structure solution and refinement. The structure was solved by direct methods (SIR92)[23] and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-93).[24] H-atoms were located in a difference map and refined freely with isotropic displacement parameters. The weighting scheme was $w^{-1} = \sigma^2(F_o^2) + (0.0483P)^2 + 0.254P$ where $3P = (F_o^2 + 2F_c^2)$. The final $wR(F^2)$ was 9.34% (based on all 2455 data used for refinement) and the conventional $R(F)$ was 3.65% [based on 1915 data with $F > 4\sigma(F)$] (*R*-factors as defined in ref. 24) for 247

parameters. The final difference map extrema were +0.18 and −0.17 e Å^{-3}, and the final shift/esd was 0.001.

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/203.

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