The Synthesis of Pyrido[4,3-*b*]carbazoles from Diphenylamine Derivatives: Alternative Routes to and Relay Syntheses of Ellipticines and Olivacines

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Two new synthetic routes to pyrido[4,3-*b*]carbazoles are described. In the first, Goldberg-type coupling of various aryl sulfonamides with aryl bromides in the presence of copper and potassium carbonate gives *N,N*-diaryl sulfonamides. UV irradiation of these, in ethanol, removes the toluene-*p*-sulfonyl protecting groups and cyclises the diphenylamine moiety to the corresponding carbazoles. These carbazoles are established intermediates in the synthesis of several ellipticines (5,11-dimethylpyrido[4,3-*b*]carbazoles).

In a complementary route, a series of substituted acetanilides are similarly coupled under Goldberg conditions with 2-bromo-5-cyanotoluene to give the corresponding cyanodiphenylamines and diphenylamides. Hydrolysis of the latter gives the diphenylamines which are then oxidatively cyclised to 3-cyano-1-methylcarbazoles. Reduction of the cyanocarbazoles leads to 3-formylcarbazoles which are known intermediates for the synthesis of 5-methylpyrido[4,3-*b*]carbazoles.

In earlier papers[1-3] we have described the synthesis of novel alkoxy-substituted ellipticines **1** essentially by 'type D'[4] pathways which have started from appropriately substituted indoles. Many of these indoles have been expensive or commercially unobtainable, and have themselves required lengthy syntheses, which have detracted from the yields and accessibilities of the final products. We now describe alternative routes to both ellipticines **1** and olivacines **2** which begin with simple, readily available benzene derivatives and involve either the photochemical cyclisation and concomitant deprotection of *N,N*-diaryl sulfonamides **3** to carbazoles **4**, or palladium(II) acetate cyclisation of cyanodiphenylamines **5** to cyanocarbazoles **6** as the key step.

The Photochemical Route to Substituted Carbazoles.—The photochemical cyclisation of diphenylamines to dihydrocarbazoles with rapid aromatisation to carbazoles, is well known,[5] but although the synthesis of diphenylamines is relatively easy from suitably activated aryl halides and amines, a more general method, applicable to alkoxy-substituted diphenylamines is the 'Goldberg' coupling reaction,[6] using an aryl bromide **7** and anilide **8** in the presence of copper. A systematic study of this reaction will be the subject of a future paper, but in this work we used (a) substituted sulfonamides **9** and (b) the acetanilides **8** to achieve coupling with aryl bromide in the presence of activated copper bronze or copper(I) species. In the cases of (a) we obtained mainly the *N,N*-diaryl sulfonamides **3** and for (b), both the diphenylamines **5** and their corresponding amides **10**.

For the sulfonamides **3** reaction occurred over activated copper bronze, in the presence of potassium carbonate from 4–24 h without solvent, at temperatures from 150–200 °C. Yields, which were not optimised, are shown in Table 1. In general, it is possible to achieve coupling *via* the alternative arrangements of bromide and sulfonamide in the starting materials, although the yields and products may be different. For example, the sulfonamide **3e** was prepared either from the bromide **7d** and sulfonamide **9a** (73%) or from bromide **7b** and sulfonamide **9d** (28%). In the case of the sulfonamide **3d**, obtained from bromide **7b** and sulfonamide **9c** (45%), an attempted preparation from the bromide **7g** and sulfonamide **9a** gave only the corresponding amine **11a**.

Table 1 Synthesis of *N,N*-diaryl sulfonamides **3**

Starting materials			
Bromide **7**	Sulfonamide **9**	Product **3**	Yield[a] (%)
a	**a**	**a**	16
b	**b**	**b**	67
c	**a**	**c**	63
b	**c**	**d**	45
d	**a**	**e**	73
b	**d**	**e**	28
e	**a**	**f**	52
b	**e**	**g**	16
f	**e**	**h**	67
b	**g**	i	35

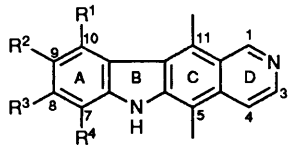
[a] After chromatography.

Exceptionally, coupling of the sulfonamide **9f** with the bromide **7f** gave, after 61 h, the triarylamine **12** (25%).

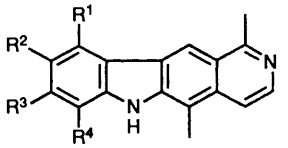
Finally, in the case of the coupling of sulfonamide **9e**, the *N*-methyl sulfonamide **13** was a significant by-product (11%). A similar transfer of methyl group from oxygen to nitrogen has been observed in the coupling of the sulfonamide **9a** with the bromide **7c**.

Attempted hydrolysis of the model sulfonamide **3h** gave only the aldehyde **3j** (84%) with hydrobromic acid in acetic acid. The use of sodium bis(2-methoxyethoxy)aluminium hydride[8] gave only a low yield of the relatively impure amine **14**. The use of this reagent for the sulfonamides **3c** and **3f** gave varying yields of the amines **11c** and **11b** (45 and 13%, respectively), but the products were impure.

In earlier work[6c,9] however, direct photochemical conversion of the acetamides **15** and **16** into the carbazoles **4a** and **b** was achieved, but these were minor components and were accompanied by larger amount of photo-Fries products. In the case of the sulfonamides **3** it proved possible to effect direct cyclisation to the carbazoles **4** with, generally, no or very minor quantities



1



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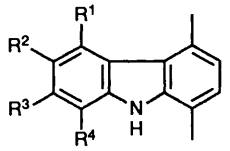
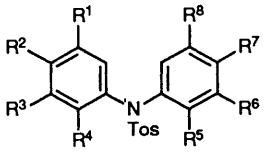


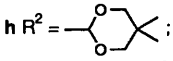
4

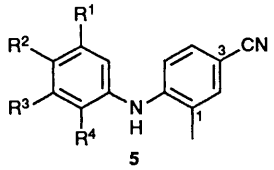
a R^2 = OMe; R^1 = R^3 = R^4 = H
b R^1 = OMe; R^2 = R^3 = R^4 = H
c R^1 = R^2 = R^3 = R^4 = H
d R^1 = R^2 = R^3 = H; R^4 = OMe
e R^1 = R^3 = OMe; R^2 = R^4 = H
f R^1 = R^3 = H; R^2 = R^4 = OMe
g R^1 = R^2 = R^3 = OMe; R^4 = H
h R^3 = OMe; R^1 = R^2 = R^4 = H
i R^1 = R^4 = H; R^2,R^3 = OCH_2O



3

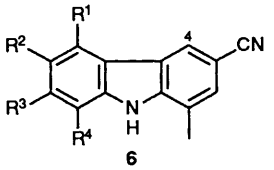
R^n = H unless stated otherwise

a R^5 = R^8 = Me
b R^1 = R^4 = Me; R^5 = OMe
c R^3 = OMe; R^5 = R^8 = Me
d R^2 = OMe; R^5 = R^8 = Me
e R^1 = R^3 = OMe; R^5 = R^8 = Me
f R^2 = R^4 = OMe; R^5 = R^8 = Me
g R^1 = R^4 = Me; R^6 = R^7 = R^8 = OMe
h R^2 =  ; R^6 = R^7 = R^8 = OMe
i R^1 = R^4 = Me; R^6,R^7 = OCH_2O
j R^2 = CHO; R^6 = R^7 = R^8 = OMe



5

a R^1 = R^3 = OMe; R^2 = R^4 = H
b R^1 = R^2 = R^3 = R^4 = H
c R^2 = OMe; R^1 = R^3 = R^4 = H
d R^1 = R^2 = R^3 = OMe; R^4 = H
e R^1 = R^4 = H; R^2,R^3 = OCH_2O



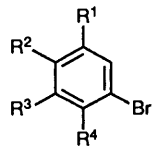
6

a R^1 = R^2 = R^3 = R^4 = H
b R^2 = OMe; R^1 = R^3 = R^4 = H
c R^1 = R^2 = R^3 = OMe; R^4 = H
d R^1 = R^3 = OMe; R^2 = R^4 = H

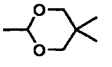
of by-products. Typically the starting material was irradiated for 7 h at a concentration of *ca.* 3 mmol dm^{-3} in ethanol under nitrogen using a medium pressure mercury vapour lamp (see Table 2).

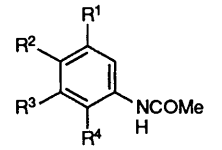
The carbazoles obtained as described above were, in few cases, accompanied by by-products which will be discussed below, but in general they were easily separated. For the carbazoles **4a**,[10] **c**,[9] **d**,[11] **f**,[3] **g**[1] and **i**[12] subsequent conversions into the corresponding ellipticines **1** have already been described,[1,3,9–12] using well-established methods[13] for annulation of ring D, so that the sulfonamide–bromide coupling and photochemical cyclisation–deprotection sequence constitutes a novel, simplifed relay synthesis of all these ellipticines.

In the case only of the sulfonamide **3b** was the main product **4d** accompanied by 3% of the photo-Fries product **17**. The compound showed M^+ 381.1399 ($C_{22}H_{23}NO_3S$) and in its NMR spectrum, NOE difference spectra showed that saturation of the OMe group at δ 3.96 gave a 15% enhancement of the



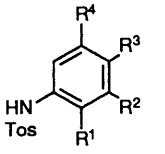
7

a R^1 = R^2 = R^3 = R^4 = H
b R^2 = R^3 = H; R^1 = R^4 = Me
c R^1 = R^2 = R^4 = H; R^3 = OMe
d R^2 = R^4 = H; R^1 = R^3 = OMe
e R^1 = R^3 = H; R^2 = R^4 = OMe
f R^1 = R^3 = R^4 = H; R^2 = 
g R^1 = R^3 = R^4 = H; R^2 = OMe



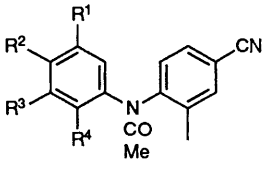
8

a R^1 = R^3 = OMe; R^2 = R^4 = H
b R^1 = R^2 = R^3 = R^4 = H
c R^1 = R^3 = R^4 = H; R^2 = OMe
d R^1 = R^2 = R^3 = OMe; R^4 = H
e R^1 = R^4 = H; R^2,R^3 = OCH_2O



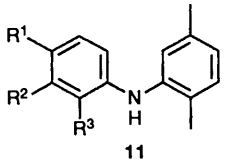
9

a R^2 = R^3 = H; R^1 = R^4 = Me
b R^2 = R^3 = R^4 = H; R^1 = OMe
c R^1 = R^2 = R^4 = H; R^3 = OMe
d R^1 = R^3 = H; R^2 = R^4 = OMe
e R^1 = H; R^2 = R^3 = R^4 = OMe
f R^2 = R^4 = H; R^1 = R^3 = OMe
g R^1 = R^4 = H; R^2 = R^3 = OCH_2O



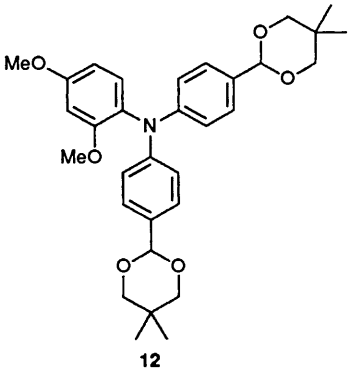
10

a R^1 = R^3 = OMe; R^2 = R^4 = H
b R^1 = R^2 = R^3 = R^4 = H
c R^1 = R^3 = R^4 = H; R^2 = OMe
d R^1 = R^2 = R^3 = OMe; R^4 = H
e R^1 = R^4 = H; R^2,R^3 = OCH_2O



11

a R^1 = OMe; R^2 = R^3 = H
b R^1 = R^3 = OMe; R^2 = H
c R^1 = R^3 = H; R^2 = OMe



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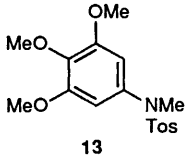

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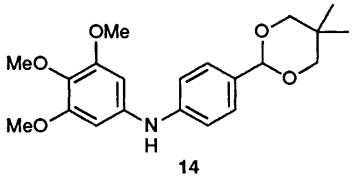

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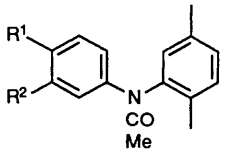


15 R^1 = OMe; R^2 = H
16 R^1 = H; R^2 = OMe

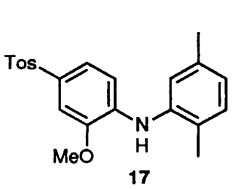
singlet signal at δ 7.33, showing the position of the toluene-*p*-sulfonyl group.

It is of interest that irradiation of the sulfonamide **3h** gave only the photo-Fries product **18** (27%), (M^+, 528.2056. C_{28}-

Table 2 Yields, after chromatography, of carbazoles **4** from diaryl sulfonamides **3**

Sulfonamide 3	Carbazole 4	Yield[a] (%)
a	**c**	54
d	**a**	73
b	**d**	34
c	**b**	25
e	**e**	43
f	**f**	23
g	**g**	15
i	**i**	24

[a] After chromatography.



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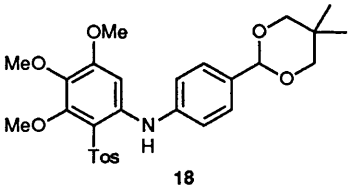
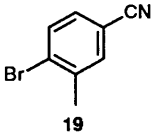


18



19

$H_{34}NO_7S$). The position of the rearranged toluene-*p*-sulfonyl group was evident from its ^1H NMR spectrum which showed an AB quartet remaining for the right-hand ring of **18** and a 1H-intensity singlet at δ 6.53 due to the remaining aromatic proton of the left-hand ring.

The Palladium(II) *Acetate Route to Substituted Carbazoles.*—(a) *Synthesis of the cyanodiphenylamines.* Another strategy for the preparation of key carbazoles for pyrido[4,3-*b*]carbazole synthesis lay potentially in the palladium(II) acetate oxidation of diphenylamines, on which a preliminary report appeared[14] in 1975. This pathway would require the free diphenylamine and the ease of hydrolysis of amides, compared with sulfonamides, suggested that we should couple acetanilides with bromobenzene derivatives.

In our earlier modification[13b] of the Pomeranz–Fritsch cyclisation, we annulated ring D of the pyrido[4,3-*b*]carbazole system by first introducing the necessary formyl groups at the carbazole 3-position. This formylation step may often lack regiospecificity as has been found in some instances in which ring A is substituted by activating groups. For example in the cases of the carbazoles **4h**,[10] and **4f**,[3] Vilsmeier formylation took place exclusively in ring A, and in carbazole **4g** a mixture of ring A and C formylation occurred.[1] In the light of some preliminary work[6c] we chose the cyano group as an alternative to the formyl group expecting that this would be stable to the conditions of Goldberg coupling and to the palladium(II) acetate oxidation. It could be converted into the formyl group (or possibly the aminomethyl group) by subsequent reduction.

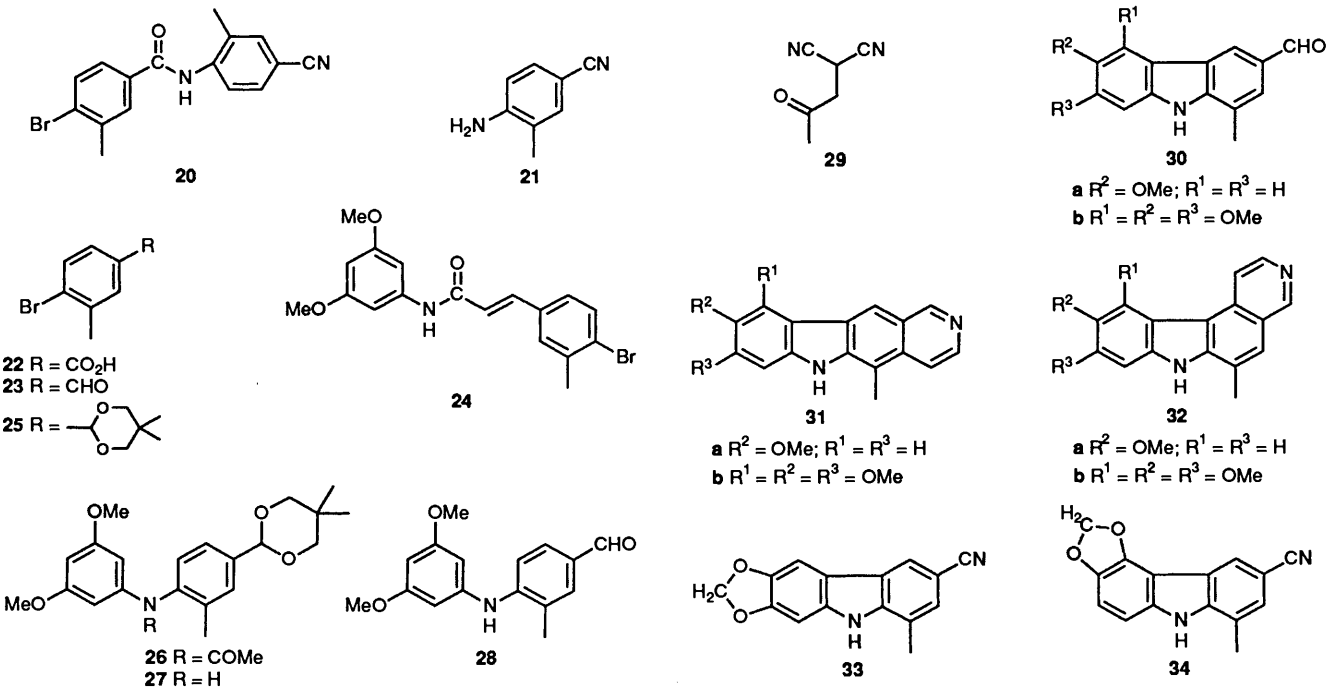
In our first experiments we coupled equimolar amounts of the anilide **8a** and the bromomethyl nitrile **19**[15] at 160–170 °C in the presence of activated copper bronze and anhydrous potassium carbonate. Under these conditions, the desired cyanodiphenylamine **5a** was obtained, but in only very low yield (6%). Its structure followed unambiguously from its spectra and microanalysis. A very low yield of a colourless crystalline solid, m.p. 180 °C was also isolated. The IR spectrum showed both the cyanide (2230 cm^{-1}) and an amide group (1650 cm^{-1}). Mass spectrometry confirmed the molecular formula as $C_{16}H_{13}BrN_2O$. The six aromatic proton signals in the ^1H NMR spectrum were consistent with the structure **20**. The amide appeared to have been formed by substitution of the activated bromine followed by hydration, and indeed, when the nitrile **19** was heated with activated copper bronze and potassium carbonate for 10 h the crude anilide **20** was formed in 20% yield. Recrystallisation gave a sample of the same amide, m.p. 180 °C; ν_{max}(Nujol)/cm^{-1} 1650. Concentration of the mother liquors, however gave a solid, m.p. 136–137 °C, ν_{max}/cm^{-1} 1680. Apart from these differences all other spectral data on these samples were identical. It would appear that the two solids were different rotamers about the C–N bond. Treatment of amide **20** with ethanolic potassium hydroxide gave the amine **21**,[16] and the acid **22**.[17] If a 3:1 molar excess of the anilide **8a** to nitrile **19** was used, none of the nitrile **20** was obtained, the major product (26%) being the diphenylamide **10a** but if copper(I) oxide at 190–200 °C was used in place of copper bronze for 7 h, the yield of the amide **10a** was increased to 72%. It is of interest that copper(I) bromide, under the same conditions, gave only a 28% yield. The amide **10a**, in its ^1H NMR spectrum, gave only broad signals, even at 100 °C, presumably due to hindered rotation. This was a general feature of the spectra of the amides **10**. Hydrolysis with ethanolic potassium hydroxide gave the pure amine **5a** in 95% yield.

In contrast to the nitrile **19**, when the aldehyde **23**[15b] was heated for 6 h at 180–200 °C with copper(I) oxide and the anilide **8a** only the bromocinnamide **24** (53%) was isolated after chromatography. The mass spectrum (M^+, 375.377) and elemental analysis supported structure **24** and the bridging group was evident from the IR spectrum (3300, 1680 and 1630 cm^{-1}) and the ^1H NMR spectrum which showed the vinyl protons as two doublets, J 14 Hz, at δ 7.66 and 6.53. In an attempt to avoid aldol condensation between the anilide **8a** and the aldehyde **23** the latter was converted into its acetal **25** in 98% yield. The acetal **25** and the anilide **8a** were coupled at 185–195 °C with activated copper bronze to give the diphenylamide **26** (36%).

Alkaline hydrolysis of the diphenylamide **26** gave the amine **27** (65%) which on acid hydrolysis in aqueous dioxane afforded a 49% yield of the amine **28**. A more direct route to this amine (79%) proved to be reduction of the nitrile **5a** with diisobutylaluminium hydride in toluene.

Having successfully obtained the 3,5-dimethoxyphenylaniline **5a**, the anilides **8b–8e** were coupled with the nitrile **19**. Hogan, Jenkins and Sainsbury recently reported[18] a synthesis of the alkaloid olivacine **2** (R^1–R^4 = H) in which the 3-cyano-1-methylcarbazole **6a**, a key intermediate synthesised from gramine and the 2-cyano-4-oxopentanonitrile **29**, was reduced to the corresponding aldehyde, which was in turn annulated by several steps to olivacine. One advantage of this approach was the regiospecific introduction of the 1-methyl and 3-cyano groups in the carbazole. The route however, would require gramines substituted in the indole nucleus for application to ring A-substituted derivatives of olivacine **2** (R^1–R^4 = H). In our route, the bromobenzonitrile **19** and acetanilide, gave the amine **5b** (9.5%) and the amide **10b** (15%). With copper(I) oxide instead of copper bronze, a slightly improved yield of the amide (20%) was achieved, but with none of the corresponding amine.

Virtually quantitative hydrolysis of the amide **10b** to the amine **5b** was achieved with potassium hydroxide in refluxing ethanol in 1 h. Similarly, 4-methoxyacetanilide, when coupled with the nitrile **19**, gave, apart from starting materials, only the amine **5c** (9%) and amide **10c** (36%). The use of copper(I) oxide gave a very similar yield of the amide, but less amine, whereas copper(I) chloride gave only trace amounts of each product. Similar couplings of the nitrile **19** with 3,4,5-trimethoxyacetanilide **8d** in the presence of copper(I) oxide gave the corresponding amine **5d** and amide **10d** in yields of 5 and 21%



respectively. As before, quantitative hydrolysis of the amide to the amine was possible.

Finally, coupling of the nitrile **19** with 3,4-methylenedioxyacetanilide **8e** was examined using both copper bronze and copper(I) oxide. With the former, besides the expected amine **5e** and amide **10e** and unused starting materials, 4-cyano-2-methylaniline[16] **21** was isolated. This may have arisen by *in situ* formation and hydrolysis of the amide **20** (see above).

The use of a 3:1 molar excess of starting amide **8e** to the nitrile **19** together with rigorous drying of materials and glassware failed to irradicate the formation of the amine **21**. Neither the nitrile **20** nor the acid **22** were detected in the mixture of products. The use of copper(I) oxide afforded only a very small yield of amine **5e** and amide **10e**.

Although the combined yields of amines + amides in these Goldberg couplings were variable, the easy availability of starting materials and the ready and virtually quantitative hydrolysis of the amides to the amines made the reactions a simple and convenient route to the diphenylamine precursors for the formation of 3-cyanocarbazoles. No attempts were made, however, to optimise the yields of coupling products and it is clear that the change from copper to copper(I) oxide [or copper(I) chloride] has potentially a dramatic if unpredictable effect on the course and yield of the reactions.

Cyclisation of Diphenylamines to 3-Substituted Carbazoles with Palladium(II) *Acetate*.—With the accessibility of the substituted 1-methyl-*N*-phenylanilines **5a–e**, we next examined their cyclisations to carbazoles. The diphenylamine **5b** on heating at reflux in trifluoroacetic acid under nitrogen for 2 h with one mole of palladium acetate gave 3-cyano-1-methylcarbazole[18] **6a** (30%) as the only isolable product.

As this carbazole had been synthesised previously[18] we did not attempt to optimise the yield. In the case of the diphenylamine **5c**, however, the best conditions (50% yield) appeared to be 2 equiv. of palladium(II) acetate in refluxing trifluoroacetic acid for 2.25 h under nitrogen. Reduction of the resulting nitrile **6b** with diisobutylaluminium hydride in diglyme gave the corresponding aldehyde **30a**.[19] Viel *et al.*[19] synthesised this formylcarbazole **30a** from *p*-methoxyphenylhydrazone and 2-methylcyclohexanone, and then[19,20] annulated the pyridine ring to the pyridocarbazoles **31a** and **32a** so that the present work constitutes a relay synthesis of these systems. Reissert alkylation of the isoquinoline moiety of the pyrido[4,3-*b*]-carbazole **31a** would also be expected to give 9-methoxyolivacine **2** (R^2 = OMe, R^1 = R^3 = R^4 = H) by analogy with earlier work.[21]

The diphenylamine **5d** was oxidised by palladium(II) acetate in refluxing acetic acid to give the cyanocarbazole **6c** in 57% yield. The UV spectrum was characteristic of a cyanocarbazole and in the ^{1}H NMR spectrum, the 4-H proton, as expected, gave a singlet at δ 8.34. Reduction of the nitrile **6c** with diisobutylaluminium hydride in diglyme gave the 3-formylcarbazole **30b** (69%). The facile synthesis of this carbazole enables an alternative synthesis of the pyridocarbazole systems **31b** and **32b**. Similarly, oxidation of the diphenylamine **5e**, gave a mixture of the isomeric carbazoles **33** and **34** in the ratio of 6:1 respectively, 45% after chromatography. That the major isomer was **33** was evident from the two intense singlets at δ 7.66 and 7.05 from the 5- and 8-protons, respectively, and the minor AB system of doublets at δ 7.13 and 7.04.

Finally, the diphenylamine **5a** on treatment with 2 equiv. of palladium(II) acetate in acetic acid at reflux for 1 h gave the carbazole **6d** in 55% yield. The synthesis of pyridocarbazoles from this dimethoxycarbazole presented difficulties and interesting aspects which will be discussed in a future paper.

The approach to the pyridocarbazole system has been achieved in a number of cases previously which were based on the appropriate indoles as starting materials and their conversion into the 1,4-dimethylcarbazoles with hexane-2,5-dione. The present results offer viable and simpler alternative routes to the appropriate intermediate carbazoles or formylcarbazoles through photochemical cyclisation and deprotection of diphenylsulfonamides, or palladium acetate oxidation of the free cyanodiphenylamines. These methods are particularly valuable for the pyridocarbazoles substituted only in the 5- and not the 11-position. For pyridocarbazoles in which ring A contains electron-donating substituents, *in situ* introduction of the nitrile group specifically *via* the unit **19** into the carbazole 3-position avoids the problem of the lack of regiospecificity during formylation of the carbazole unsubstituted at position 3.

Experimental

M.p.s were uncorrected. UV spectra were measured on a Unicam SP-800 spectrophotometer or a Jasco model 7850 spectrometer. ^{1}H NMR spectra, unless stated otherwise, were recorded in deuterochloroform on a Bruker 360 MHz spectrometer, *J* values are given in Hz. Column chromatography was performed on Merck silica gel 60 (Art 9385) or (Art 7729). Light petroleum refers to solvent boiling in the range 40–60 °C.

Goldberg Coupling Reactions.—(a) *Sulfonamides. Activation of the copper.* Copper bronze (10 g) was treated with a 2% solution of iodine in acetone (100 cm^3) for 5–10 min. It was filtered and washed by stirring with a 1:1 solution of concentrated hydrochloric acid in acetone (50 cm^3). The residual copper bronze was filtered at the pump, washed with acetone and dried in a vacuum desiccator.

Potassium carbonate was dried overnight at 120 °C.

Method (a). 2,5-*Dimethyl*-N-*phenyl*-N-(*toluene*-p-*sulfonyl*)*aniline* **3a**. The aryl bromide **7a** (7 g, 0.046 mol), and sulfonamide **9a** (8 g, 0.029 mol), copper bronze (4.5 g) and potassium carbonate (1.5 g) were heated at reflux for 13 h. To the cooled mixture water was added and the excess of bromide **7a** was removed by steam distillation. The cooled aqueous residue was extracted with ether (3 × 100 cm^3 + 4 × 50 cm^3) and the combined ether extracts were dried ($MgSO_4$). Removal of solvent gave a brown oil (2.55 g). Part of this oil was submitted to flash chromatography (ethyl acetate–light petroleum, 5:95) and gave a light pink solid (0.66 g, scaled up yield 16.5%). Crystallisation from ethyl acetate–light petroleum afforded the pure *sulfonamide* **3a** as colourless crystals, m.p. 119–121 °C; δ_H(60 MHz) 2.22 (6 H, s, 2 × Ar-CH_3), 2.40 (3 H, s, Ar-CH_3) and 6.80–7.90 (12 H, m, Ar-H); λ_{max}(EtOH)/nm 213 (ε/dm^3 mol^{-1} cm^{-1} 23 130); *m/z* (%) (EI) 351 (M^+, 24), 196 (100), 181 (60) and 180 (45) (Found: C, 71.6; H, 6.0; N, 3.65. $C_{21}H_{21}NO_2S$ requires C, 71.8; H, 6.02; N, 3.99%).

Method (b). N-(2′-*Methoxyphenyl*)-2,5-*dimethyl*-N-(*toluene*-p-*sulfonyl*)*aniline* **3b**. The sulfonamide **9b** (1.5 g, 0.0054 mol), the aryl bromide **7b** (1.2 g, 0.0065 mol), copper bronze (0.75 g) and potassium carbonate (0.3 g) were heated at reflux (200 °C) for 10.5 h. The cooled mixture was treated with chloroform and the copper and potassium carbonate were removed by filtration before the residue was submitted to flash chromatography (ether–light petroleum, 25:75) and gave a solid (1.38 g, 67%), m.p. 116–118 °C. Crystallisation from ether–light petroleum gave the *sulfonamide* **3b** as colourless crystals, m.p. 120.5–122 °C; δ_H 2.26 (3 H, s, 2-Me), 2.34 (3 H, s, 5-Me), 2.45 (3 H, s, tosyl-Me), 3.61 (3 H, s, OMe), 6.84 (1 H, d, *J* 8, 3′-H), 6.90 (1 H, dt, *J* 8, 1.5, 5′-H), 7.00 (1 H, d, *J* 8, 4-H), 7.07 (1 H, d, *J* 8, 3-H), 7.24 (4 H, m, 4′- and 6-H and 3- and 5-H of tosyl), 7.44 (1 H, dd, *J* 8, 1.5, 6′-H) and 7.58 (2 H, d, *J* 8, 2- and 6-H of tosyl); *m/z* (%) (EI) 381 (M^+, 10), 226 (100), 194 (90), 91 (60) and 65 (30); (CI) 382 (M^+ + 1, 60) and 227 (100).

N-(3′-*Methoxyphenyl*)-2,5-*dimethyl*-N-(*toluene*-p-*sulfonyl*)*aniline* **3c**. The aryl bromide **7c** (3.8 g, 0.02 mol), the sulfonamide **9a** (2.75 g, 0.01 mol), copper bronze (1.5 g) and potassium carbonate (0.5 g) were heated at reflux under nitrogen for 4 h. Work-up by method (a) gave a dark brown oil (3.86 g) which on flash chromatography (ethyl acetate–light petroleum, 15:75) gave the main product as a light yellow solid (2.4 g, 63%), m.p. 75–77 °C. This was crystallised from ethanol to give the sulfonamide **3c** as colourless crystals, m.p. 79–80 °C (lit.,[6c] 77–78.5 °C); δ_H(60 MHz) 2.20 (6 H, s, 2 × Ar-Me), 2.40 (3 H, s, Ar-Me), 3.70 (3 H, s, OMe) and 6.50–7.80 (11 H, m, Ar-H); λ_{max}(EtOH)/nm 221 (ε/dm^3 mol^{-1} cm^{-1} 28 180), 270 (6250) and 278 (5977).

N-(4′-*Methoxyphenyl*)-2,5-*dimethyl*-N-(*toluene*-p-*sulfonyl*)*aniline* **3d**. The sulfonamide **9c** (1 g, 0.0038 mol), the aryl bromide **7b** (0.84 g, 0.0046 mol), copper bronze (0.5 g) and potassium carbonate (0.2 g) were heated at reflux (200 °C) for 4 h. Work-up by method (b) gave an oil (1.7 g) which on chromatography (ether–light petroleum, 20:80) gave a colourless solid (0.4 g), m.p. 151–152 °C and a more impure fraction (total yield 45%) which was crystallised from ether to give the *sulfonamide* **3d** as colourless crystals, m.p. 152–153 °C; δ_H 2.25 (3 H, s, 2-Me), 2.31 (3 H, s, 5-Me), 2.46 (3 H, s, tosyl-Me), 3.78 (3 H, s, OMe), 6.81 (2 H, d, *J* 9, 3′- and 5′-H), 6.88 (1 H, s, 6-H), 7.02 (1 H, d, *J* 7.5, 4-H), 7.11 (1 H, d, *J* 7.5, 3-H), 7.25 (2 H, d, *J* 9, 2′- and 6′-H), 7.27 (2 H, d, *J* 8, 3- and 5-H of tosyl) and 7.57 (2 H, d, *J* 8, 2- and 6-H of tosyl); *m/z* (%) (EI) 381 (M^+, 10), 226 (100), 194 (60), 91 (50) and 65 (23); (CI) 382 (30) and 227 (100) (Found: C, 69.4; H, 6.1; N, 3.6. $C_{22}H_{16}NO_3S$ requires C, 69.3; H, 6.08; N, 3.67%).

N-(4′-*Methoxyphenyl*)-2,5-*dimethylaniline* **11** (*attempted preparation of the sulfonamide* **3d**). The aryl bromide **7g** (3.8 g, 0.02 mol), the sulfonamide **9a** (2.7 g, 0.0098 mol), copper bronze (1.5 g) and potassium carbonate (0.5 g) were heated at reflux for 1.5 h. Work-up by method (a) gave a brown oil (1.5 g) which was submitted to flash chromatography (ethyl acetate–light petroleum, 1:99) and gave the still impure product (0.4 g). Crystallisation of 0.2 g from light petroleum gave the amine **11** as a cream solid (110 mg, scaled up yield 10%), m.p. 34–35 °C (lit.,[9] oil); δ_H(60 MHz) 2.20 (6 H, s, 2 × Ar-Me), 3.74 (3 H, s, OMe), 5.10 (1 H, br s, NH) and 6.40–7.30 (7 H, m, Ar-H); λ_{max}(EtOH)/nm 210 (ε/dm^3 mol^{-1} cm^{-1} 21 950) and 282 (15 050); ν_{max}(Nujol mull)/cm^{-1} 3400 (sh, NH); *m/z* (%) (EI) 228 (M^+ + 1, 14), 227 (M^+, 94), 213 (16), 212 (100) and 72 (12) (Found: M^+, 227.1302. $C_{15}H_{17}NO$ requires *M*, 227.1310).

N-(3′,5′-*Dimethoxyphenyl*)-2,5-*dimethyl*-N-*toluene*-p-*sulfonylaniline* **3e**. First preparation. The sulfonamide **9d** (1 g, 0.0033 mol), the aryl bromide **7b** (0.723 g, 0.0039 mol), copper bronze (0.59 g) and potassium carbonate (0.2 g) were heated at 180 °C for 6 h and at 200 °C for 12 h. Work-up by method (b) gave a brown oil (1.6 g) which on chromatography (ether–light petroleum, 40:60) gave a pink oil (0.290 g, 21%) which crystallised from ether–light petroleum to give pink crystals, m.p. 110–112 °C. Recrystallisation from ether gave the *sulfonamide* **3e** as colourless crystals, m.p. 118.5–119 °C; δ_H 2.24 (6 H, s, 2-Me and Tos-Me), 2.43 (3 H, s, 5-Me), 3.72 (6 H, s, 2 × OMe), 6.27 (1 H, s, 4′-H), 6.46 (2 H, s, 2′- and 6′-H), 6.87 (1 H, s, 6-H), 7.05 (1 H, d, *J* 7, 4-H), 7.13 (1 H, d, *J* 7, 3-H), 7.29 (2 H, d, *J* 8, 3- and 5-H of tosyl) and 7.66 (2 H, d, *J* 8, 2- and 6-H of tosyl); λ_{max}(EtOH)/nm 204 (ε/dm^3 mol^{-1} cm^{-1} 45 132) 267infl (4375) and 276infl (3593) (Found: C, 66.9; H, 6.25; N, 3.5. $C_{23}H_{25}NO_4S$ requires C, 67.1; H, 6.12; N, 3.40%).

Taking into account another fraction (0.1 g), shown to be the product **3e** in a reasonably pure form, the yield rose to 28%.

Second preparation. The aryl bromide **7d** (1.94 g, 0.0089 mol), the sulfonamide **9a** (1.6 g, 0.006 mol), copper bronze (0.8 g) and potassium carbonate (0.25 g) were heated at 130–200 °C for 7 h. Work-up as for the first preparation gave a brown oil (3.7 g). This oil was submitted to vacuum filtration through a column using solvent mixtures of increasing polarity, from dichloromethane–light petroleum (3:7 to pure dichloromethane) to give an oil (1.83 g, 73%). Crystallisation from dichloromethane–light petroleum gave **3e** as colourless crystals, m.p. 120–121 °C. The TLC and NMR spectrum were identical to those from the first preparation.

N-(2′,4′-*Dimethoxyphenyl*)-2,5-*dimethyl*-N-*toluene*-p-*sulfonylaniline* **3f**. The aryl bromide **7e** (3.6 g, 0.0165 mol), the sulfonamide **9a** (3 g, 0.011 mol), copper bronze (1.5 g) and potassium carbonate (0.5 g) were heated at 175 °C under an atmosphere of nitrogen for 24 h. Work-up by method (b) gave a brown oil (5.98 g). Chromatography (ethyl acetate–light petroleum, 2:8) gave two oily fractions (2.12 and 1.16 g) each of which solidified, m.p. 85–87 and 70–74 °C, respectively (73%). Crystallisation of the two combined fractions, from ethyl

acetate–light petroleum afforded the *sulfonamide* **3f** as colourless crystals (2.34 g, 52%), m.p. 89–91 °C; δ_H 2.23 (3 H, s, Me), 2.37 (3 H, s, Me), 2.43 (3 H, s, Me), 6.36 (1 H, d, *J* 2.5, 3′-H), 6.42 (1 H, dd, *J* 8.5, 2.5, 5′-H), 6.98 (1 H, br d, *J* 8, 4-H), 7.07 (1 H, d, *J* 8, 3-H), 7.20 (1 H, br s, 6-H), 7.24 (2 H, d, *J* 8, 2 × Ar-H of tosyl), 7.36 (1 H, d, *J* 8.5, 6′-H) and 7.56 (2 H, d, *J* 8, 2 × Ar-H of tosyl); λ_{max}(EtOH)/nm 215 (ε/dm^3 mol^{-1} cm^{-1} 25 370) and 280 (5930); *m*/*z* (%) (EI) 412 (M^+ + 1, 3), 411 (M^+, 11), 257 (20), 256 (100), 225 (39) and 224 (47) (Found: M^+, 411.1507. $C_{23}H_{25}NO_4S$ requires *M*, 411.1504) (Found: C, 67.1; H, 6.0; N, 3.2. $C_{23}H_{25}NO_4S$ requires C, 67.1; H, 6.12; N, 3.40%).

N-(3′,4′,5′-*Trimethoxyphenyl*)-2,5-*dimethyl*-N-*toluene*-p-*sulfonylaniline* **3g**. The sulfonamide **9e** (1 g, 0.003 mol), the aryl bromide **7b** (0.67 g, 0.0036 mol), copper bronze (0.45 g) and potassium carbonate (0.15 g) were heated to reflux at 200 °C for 10 h. Work-up by method (b) gave a dark brown oil (1.6 g) which on chromatography (ether–light petroleum, 35:65) gave an orange oil (0.4 g) which was a mixture of two spots (TLC). This was re-chromatographed to give 100 mg of the *sulfonamide* **3g**, the 3,4,5-*trimethoxy*-N-*methyl*-N-(*toluene*-p-*sulfonyl*)*aniline* **13** (80 mg) and 200 mg of a mixture of the two products. Crystallisation of **3g** from ethanol–chloroform gave colourless crystals, m.p. 130–131.5 °C; δ_H 2.25 (3 H, s, 2-Me), 2.33 (3 H, s, 5-Me), 2.46 (3 H, s, Tos-Me), 3.74 (6 H, s, 2 × OMe), 3.82 (3 H, s, OMe), 6.50 (2 H, s, 2′- and 6′-H), 6.87 (1 H, s, 6-H), 7.06 (1 H, d, *J* 7, 4-H), 7.16 (1 H, d, *J* 7, 3-H), 7.29 (2 H, d, *J* 7.5, 3- and 5-H of tosyl) and 7.64 (2 H, d, *J* 7.5, 2- and 6-H of tosyl); λ_{max}(EtOH)/nm 218 (ε/dm^3 mol^{-1} cm^{-1} 6252), 243 (7735) and 277infl (4248); *m*/*z* (%) (EI) 441 (M^+, 10), 286 (100), 255 (97), 254 (100), 91 (72) and 42 (65); (CI) 442 (80) and 288 (100) (Found: C, 65.3; H, 6.15; N, 3.15. $C_{24}H_{27}NO_5S$ requires C, 65.3; H, 6.16; N, 3.17%).

Crystallisation of **13** from ethanol–chloroform gave colourless crystals, m.p. 147.5–148 °C; δ_H 2.45 (3 H, s, Me), 3.15 (3 H, s, N-Me), 3.75 (6 H, s, 2 × OMe), 3.85 (3 H, s, OMe), 6.30 (2 H, s, Ar-H), 7.30 (2 H, d, *J* 7, 3- and 5-H of tosyl) and 7.53 (2 H, d, *J* 7, 2- and 6-H of tosyl); *m*/*z* (%) (EI) 351 (M^+, 40) and 196 (100); (CI) 352 (100) and 197 (80).

The mixture of the two products (200 mg) was submitted to PLC (silica, ether–hexane, 1:1) and gave 60 mg of **3g** (total yield 13%) and 40 mg of **13** (total yield 12%).

A further preparation using a lower reaction temperature (7 h at 150 °C + 16 h at 180 °C) gave 16% of **3g** and 11% of **13**.

4′-(5,5-*Dimethyl*-1,3-*dioxan*-2-*yl*)-3,4,5-*trimethoxy*-N-*toluene*-p-*sulfonyldiphenylamine* **3h**. A mixture of the sulfonamide **9e** (1 g, 0.003 mol), the aryl bromide **7f** (1.63 g, 0.006 mol), copper bronze (0.45 g) and potassium carbonate (0.15 g) was heated under an atmosphere of nitrogen at 180 °C for 12 h. Work-up by method (b) gave a brown oil (2.30 g). Chromatography (ethyl acetate–light petroleum, 35:65) afforded the product **3h** as an off-white solid (1.07 g, 67%), m.p. 143–145 °C. Crystallisation from ethyl acetate–light petroleum gave the *sulfonamide* **3h** as colourless needles, m.p. 147–148 °C; δ_H 0.80 (3 H, s, CH_2-C*Me*), 1.28 (3 H, s, CH_2C*Me*), 2.45 (3 H, s, Ar-Me), 3.65 (2 H, d, *J* 13, 2 × OC*H*CMe$_2$), 3.72 (6 H, s, 3- and 5-OMe), 3.77 (2 H, d, *J* 13, 2 × OC*H*CMe$_2$), 3.80 (3 H, s, 4-OMe), 5.38 (1 H, s, Ar-CH), 6.40 (2 H, s, 2- and 6-H), 7.27 (2 H, overlapping d, *J* 8, 2 × Ar-H of tosyl *ortho* to Me), 7.30 (2 H, overlapping d, *J* 8, 3′- and 5′- or 2′- and 6′-H), 7.46 (2 H, d, *J* 8, 2′- and 6′- or 3′- and 5′-H) and 7.64 (2 H, d, *J* 8, 2 × Ar-H of tosyl *meta* to Me); λ_{max}(EtOH)/nm 224 (ε/dm^3 mol^{-1} cm^{-1} 29 400) (Found: M^+, 527.1954. $C_{28}H_{33}NO_7$ requires *M*, 527.1977).

Attempted preparation of 2,4-dimethoxy-4′-(5,5-dimethyl-1,3-dioxan-2-yl)-N-toluene-p-sulfonyldiphenylamine. The sulfonamide **9f** (1.6 g, 0.0052 mol), and aryl bromide **7f** (2.6 g, 0.0096 mol), copper bronze (0.8 g) and potassium carbonate (0.23 g) were heated under an atmosphere of nitrogen at 175 °C for 34 h. Method (b) work-up was followed by the addition of fresh copper bronze (0.4 g), potassium carbonate (0.1 g) and bromide **7f** (0.5 g, 0.0018 mol). The mixture was again heated under nitrogen at 175 °C for 27 h (total 61 h). Work-up by method (b) gave a green oil (3.63 g) which on chromatography (ethyl acetate–light petroleum, 10:90) gave a yellow oil (0.659, 25%) which solidified on cooling. Part of this oil was crystallised from chloroform–light petroleum affording the pure 2,4-*dimethoxy*-4′,4″-*bis*(5,5-*dimethyl*-1,3-*dioxan*-2-*yl*)*triphenylamine* **12** as colourless crystals, m.p. 95–97 °C; δ_H 0.79 (6 H, s, 2 × CMe), 1.30 (6 H, s, 2 × CMe), 3.59 (3 H, s, OMe), 3.63 (4 H, d, *J* 11, 4 × OC*H*CMe$_2$), 3.75 (4 H, d, *J* 11, 4 × OC*H*CMe$_2$), 3.81 (3 H, s, OMe), 5.32 (2 H, s, 2 × Ar-CH), 6.44 (1 H, dd, *J* 9, 3, 5-H), 6.50 (1 H, d, *J* 3, 3-H), 6.94 (4 H, d, *J* 9, 2′- and 6′-H and 2″- and 6″-H), 7.02 (1 H, d, *J* 9, 6-H) and 7.30 (4 H, d, *J* 9, 3′- and 5′-H and 3″- and 5″-H); λ_{max}(EtOH)/nm 210 (ε/dm^3 mol^{-1} cm^{-1} 19 980) and 301 (10 330); *m*/*z* (%) (EI) 535 (M^+ + 2, 12), 534 (M^+ + 1, 36) and 533 (M^+, 100) (Found: C, 72.0; H, 7.15; N, 2.7%; M^+, 533.2778. $C_{32}H_{39}NO_6$ requires C, 72.0; H, 7.37; N, 2.62%; *M*, 533.27768).

N-(3′,4′-*Methylenedioxyphenyl*)2,5-*dimethyl*-N-(*toluene*-p-*sulfonyl*)*aniline* **3i**. The sulfonamide **9g** (3 g, 0.01 mol), the aryl bromide **7b** (2.4 g, 0.013 mol), copper bronze (1.5 g) and potassium carbonate (0.5 g) were heated at 180 °C for 9 h. Work-up by method (b) gave an oily solid (4.8 g) which was submitted to vacuum filtration through a silica column using solvent gradient (ether–light petroleum, 20:80 to 45:55) and gave the product **3i** as an orange solid (1.13 g, 29%), m.p. 148–150 °C. Crystallisation from ether gave the *sulfonamide* **3i** as colourless crystals, m.p. 153–154 °C; δ_H 2.24 (3 H, s, Me), 2.31 (3 H, s, Me), 2.47 (3 H, s, tosyl-Me), 5.94 (2 H, s, OCH_2O), 6.70 (1 H, d, *J* 8, 5′-H), 6.79 (1 H, dd, *J* 8, 2, 6′-H), 6.85 (2 H, m, 6- and 2′-H), 7.03 (1 H, d, *J* 8, 4-H), 7.11 (1 H, d, *J* 8, 3-H), 7.26 (2 H, d, *J* 8, Ar-H of tosyl *ortho* to Me) and 7.56 (2 H, d, *J* 8, Ar-H of tosyl *meta* to Me); λ_{max}(EtOH)/nm 199 (ε/dm^3 mol^{-1} cm^{-1} 156 010), 266 (25 550) and 271 (25 930); *m*/*z* (%) (EI) 395 (M^+, 30), 240 (100), 210 (50) and 182 (60); (CI) 396 (90) and 242 (100) (Found: C, 66.7; H, 5.45, N, 3.5. $C_{22}H_{21}NO_4S$ requires C, 66.8; H, 5.35; N, 3.54%).

A further fraction was obtained (0.8 g) and it was submitted to PLC (silica, ether–light petroleum, 1:1) to give 40 mg of the pure product **3i** (total yield 35%).

Removal of the Tosyl Groups.—Attempted preparation of **14**. A mixture of the sulfonamide **3h** (50 mg, 0.095 mmol), 33% HBr in acetic acid (0.2 cm^3) and glacial acetic acid (3 cm^3) was stirred at room temperature for 3 h when a precipitate formed. The solvent was removed, water (10 cm^3) was added and the pH was adjusted to 8 with 0.2 mol dm^{-3} sodium hydroxide. The aqueous solution was extracted with ether (3 × 25 cm^3) and with ethyl acetate (2 × 25 cm^3). The two extracts were dried and the solvents were removed to give a total of 35 mg (84%) of N-4′-*formyl*-3,4,5-*trimethoxy*(*toluene*-p-*sulfonyl*)*diphenylamine* **3j**, m.p. 170–173 °C; δ_H 2.46 (3 H, s, Ar-Me), 3.74 (6 H, s, 2 × OMe), 3.88 (3 H, s, OMe), 6.41 (2 H, s, 2- and 6-H), 7.32 (2 H, d, *J* 8, 2 × Ar-H of tosyl), 7.44 (2 H, d, *J* 8, 2′-and 6′-H), 7.67 (2 H, d, *J* 8, 2 × Ar-H of tosyl), 7.82 (2 H, d, *J* 8, 3′- and 5′-H) and 9.95 (1 H, s, CHO); *m*/*z* (%) (FD) 441 (M^+, 100).

4′-(5,5-*Dimethoxy*-1,3-*dioxan*-2-*yl*)-N-3,4,5-*trimethoxyphenyldiphenylamine* **14**. The sulfonamide **3h** (0.2 g, 0.38 mol) was dissolved with stirring in dry toluene (5 cm^3). SMAH[8] {a solution of sodium bis(2-methoxyethoxy)aluminium hydride [$NaAlH_2$ $(OC_2H_4OMe)_2$] 3.4 mol dm^{-3} in toluene} (1 cm^3) was added with external cooling. The mixture was heated on a water bath (50–80 °C) with stirring, under nitrogen for 3 h. After cooling 10% aqueous sodium hydroxide solution was added dropwise (5 cm^3). The mixture was extracted with ether (4 × 5 cm^3) and the ether extracts were washed with saturated aqueous chloride (2 × 5 cm^3) and with water. The aqueous phases were

extracted again with ether (10 cm^3). The combined ether extracts were dried ($MgSO_4$) and after removal of the solvent gave a brown oil (120 mg). This was submitted to PLC (silica, ether–light petroleum, 60:40) and the *amine* **14** was obtained as a yellow oil (20 mg, 14%); δ_H(60 MHz) excluding signals due to impurities, 0.8 (3 H, s, CMe), 1.28 (3 H, s, CMe), 3.45 (1 H, br s, NH), 3.79 (13 H, s, 9 H, 3 × OMe + 4 H, 2 × OCH_2CMe_2), 5.40 (1 H, s, Ar-CH), 6.28 (2 H, s, Ar-H) and 7.00–7.50 (4 H, m, other Ar-H); $\nu_{max}(CHCl_3)/cm^{-1}$ 3763, 3590 and 3416; *m/z* (%) (EI) 243 (100).

Removal of the tosyl group from the sulfonamide **3c**. The sulfonamide **3c** (0.25 g, 0.66 mmol) was dissolved with stirring in dry toluene (5 cm^3). SMAH (0.78 cm^3, 2.64 mmol) was added. The yellow mixture was heated at reflux under nitrogen for 2.5 h and left stirring at room temperature overnight. 10% Sodium hydroxide solution (10 cm^3) was added dropwise and the mixture was extracted with ether (10 cm^3) and ethyl acetate (2 × 5 cm^3). The organic extracts were washed with saturated aqueous sodium chloride (2 × 5 cm^3), water (5 cm^3) and dried ($MgSO_4$). The solvent was removed to give a yellow oil (0.25 g). PLC (silica, ethyl acetate–light petroleum, 10:90) gave *N*-(3′-methoxyphenyl)-2,5-dimethylaniline **11c** as a light yellow oil (0.07 g, 45%); δ_H(60 MHz) 2.18 (3 H, s, Ar-Me), 2.25 (3 H, s, Ar-Me), 3.71 (3 H, s, OMe), 5.30 (1 H, br s, NH) and 6.25–7.40 (7 H, m, Ar-H). This oil solidified and the solid was washed with small portions of light petroleum to give the amine **11c** as colourless crystals, m.p. 42–44 °C; *m/z* (%) (EI) 229 (M^+ + 2, 9), 228 (M^+ + 1, 59) and 227 (M^+, 100).

Removal of the tosyl group from the sulfonamide **3f**. The sulfonamide **3f** (0.5 g, 1.2 mmol) was dissolved with stirring in dry toluene (5 cm^3). SMAH was added (1.3 cm^3, 4.3 mmol) and the mixture left stirring under nitrogen at room temperature for 5 h. 10% Sodium hydroxide solution (10 cm^3) was added dropwise and the mixture was extracted as above. The organic extracts were washed with saturated sodium chloride (2 × 5 cm^3), dried ($MgSO_4$) and combined. Removal of solvent gave a green dark oil (0.35 g) which on PLC (silica, ether–light petroleum, 1:1) gave *N*-(2′,4′-dimethoxyphenyl)-2,5-dimethylaniline **11b** as a yellow oil (40 mg, 13%); δ_H(60 MHz) 2.57 (6 H, s, 2 × Me), 3.81 (3 H, s, OMe), 3.85 (3 H, s, OMe), 5.45 (1 H, br s, NH) and 6.50–7.20 (6 H, m, Ar-H).

Photocyclisation of Diphenylsulfonamides.—General procedure. The sulfonamides **3**, *ca.* 3 mmol dm^{-3} solutions in ethanol, were irradiated for 7 h under nitrogen, using a medium pressure Hg vapour lamp. After removal of solvent the oil which was obtained was purified by flash chromatography or by PLC.

1,4-*Dimethylcarbazole* **4c**. The sulfonamide **3a** (0.2 g, 0.57 mmol) in ethanol (300 cm^3) was irradiated. The orange oil obtained on PLC (silica, chloroform–ether, 1:1) gave an off-white solid (100 mg), m.p. 75–77 °C. Crystallisation from light petroleum gave colourless crystals, m.p. 90–91 °C (lit.,[22] 97–98 °C) (60 mg, 54%) which were shown to be **4c** by comparison of NMR and UV with an authentic sample.

8-*Methoxy*-1,4-*dimethylcarbazole* **4d**.[11] The sulfonamide **3b** (0.3 g, 0.79 mmol) in ethanol (300 cm^3) gave an orange oil which on PLC (silica, dichloromethane) gave the carbazole **4d** as an oily solid (60 mg, 34%). Crystallisation from ethanol gave colourless crystals, m.p. 101–104 °C (lit.,[11] 170 °C); δ_H 2.55 (3 H, s, 1-Me), 2.87 (3 H, s, 4-Me), 4.06 (3 H, s, OMe), 6.92 (1 H, d, *J* 8, 7-H), 6.94 (1 H, d, *J* 7, 3-H), 7.13 (1 H, d, *J* 7, 2-H), 7.18 (1 H, t, *J* 8, 6-H), 7.80 (1 H, d, *J* 8, 5-H) and 8.20 (1 H, br s, NH); λ_{max}(EtOH)/nm 238 (ε/dm^3 mol^{-1} cm^{-1} 5536), 246 (5567), 249 (5584), 254 (5635), 256 (5584), 275 (4053), 285 (3794), 310infl (1617), 321 (2236) and 335 (2230); *m/z* (%) (EI) 225 (M^+, 100) and 210 (72) (Found: M^+, 225.1154. $C_{15}H_{15}NO$ requires *M*, 225.1154). A by product N-(2′-*methoxy*-4′-*toluene*-p-*sulfonylphenyl*)*aniline* **17** with a lower R_f was also isolated as an oil (9 mg, 3%); δ_H 2.16 (3 H, s, Ar-Me), 2.30 (3 H, s, Ar-Me), 2.40 (3 H, s, Me of tosyl), 3.96 (3 H, s, OMe), 6.22 (1 H, br s, NH), 6.76 (1 H, d, *J* 8, 6′-H), 6.92 (1 H, d, *J* 8, 4-H), 7.08 (1 H, s, 6-H), 7.15 (1 H, d, *J* 8, 3-H), 7.25 (2 H, partially obscured d, Ar-H of tosyl *ortho* to Me), 7.33 (1 H, s, 3′-H), 7.40 (1 H, d, *J* 8, 5′-H) and 7.80 (2 H, d, *J* 8, Ar-H of tosyl *meta* to Me). A D_2O shake removed the NH singlet at 6.22. Saturation of the ArMe protons at 2.16 enhanced the d at 7.15 by 8.5%. Saturation of the ArMe group at 2.30 enhanced the signal at 7.08 by 8% and that at 6.92 by 3%. Saturation of the signal at 3.96 (OMe) gave a 15% enhancement of the singlet at 7.33; *m/z* (%) (EI) 381 (M^+, 12), 84 (70) and 49 (100); (CI) 382 (100) (Found: M^+, 381.1399. $C_{22}H_{22}NO_3S$ requires *M*, 381.1399).

5-*Methoxy*-1,4-*dimethylcarbazole* **4b**.[6c] The sulfonamide **3c** (0.2 g, 0.53 mmol) in ethanol (300 cm^3) gave a brown oil which on PLC (silica, chloroform) gave **4b** as an oil (30 mg, 25%), identified by comparison of its NMR and UV spectra with the published [6c] data.

6-*Methoxy*-1,4-*dimethylcarbazole* **4a**.[10] The sulfonamide **3d** (0.3 g, 0.79 mmol) in ethanol (300 cm^3) gave a brown oil which on PLC (silica, dichloromethane) gave the carbazole **4a** (0.13 g, 73%), m.p. 126–129 °C. Crystallisation from EtOH gave colourless needles, m.p. 140–141 °C (lit.,[10] 140–141 °C) with identical NMR and UV data to the literature values.

5,7-*Dimethoxy*-1,4-*dimethylcarbazole* **4e**. The sulfonamide **3e** (300 mg, 0.73 mmol) in ethanol (300 cm^3) gave a brown oil which on PLC (silica, ether–light petroleum, 1:1) gave the impure carbazole as an orange oil (80 mg, 43%). Crystallisation from ethanol afforded the *carbazole* **4e** as colourless crystals (23%), m.p. 130–132 °C; δ_H 2.49 (3 H, s, 1-Me), 2.89 (3 H, s, 4-Me), 3.89 (3 H, s, OMe), 3.96 (3 H, s, OMe), 6.29 (1 H, s, 6-H), 6.55 (1 H, s, 8-H), 6.90 (1 H, d, *J* 7, 3-H), 7.01 (1 H, d, *J* 7, 2-H) and 7.94 (1 H, s br, NH); λ_{max}(EtOH)/nm 216 (ε/dm^3 mol^{-1} cm^{-1} 21 230), 248 (34 270) 285infl (7140), 292 (9000), 310 (2986) and 324 (2350) (Found: M^+, 255.1259. $C_{16}H_{17}NO_2$ requires *M*, 255.1259).

6,8-*Dimethoxy*-1,4-*dimethylcarbazole* **4f**.[3] The sulfonamide **3f** (0.2 g, 0.49 mmol) in ethanol (300 cm^3) gave an orange oil which on PLC (silica, ether–light petroleum, 5:95) gave a colourless oil (35 mg, 23%) shown to be **4f** by NMR and UV spectroscopy. Crystallisation from ethanol gave colourless crystals, m.p. 182–184 °C (lit.,[3] 186–186.5 °C).

5,6,7-*Trimethoxy*-1,4-*dimethylcarbazole* **4g**.[1] The sulfonamide **3g** (60 mg, 0.136 mmol) in ethanol (300 cm^3) gave a brown oil which on PLC (silica, ether–hexane, 1:1) gave the carbazole **4g** (6 mg, 15%) as an orange oil whose spectroscopic data (NMR and UV) were identical to those from the literature.[1]

6,7-*Methylenedioxy*-1,4-*dimethylcarbazole* **4i**.[23] The sulfonamide **3i** (0.3 g, 0.8 mmol) in ethanol gave a brown oil which on PLC (silica, dichloromethane) gave the carbazole **4i** as an orange solid (45 mg, 24%), m.p. 148–150 °C. Crystallisation from ethanol gave colourless crystals, m.p. 157.5–158.5 °C (lit.,[23] 158–160 °C); δ_H 2.50 (3 H, s, 1-Me), 2.78 (3 H, s, 5-Me), 6.02 (2 H, s, CH_2O), 6.88 (1 H, d, *J* 8, 3-H), 6.91 (1 H, s, 8-H), 7.05 (1 H, d, *J* 8, 2-H), 7.58 (1 H, s, 5-H) and 7.88 (1 H, br s, NH); λ_{max}(EtOH)/nm 208, 237, 271, 305, 333 and 347.

Attempted cyclisation of **3h**. The sulfonamide **3h** (0.3 g, 0.57 mmol) in ethanol (300 cm^3) was irradiated for 4.5 h under nitrogen. The orange oil obtained was submitted to vacuum filtration through a column using solvent gradient (ether–light petroleum, 1:9 to 5:5) and gave the photo-Fries product **18** as an oil (80 mg, 27%); δ_H 0.82 (3 H, s, CMe), 1.32 (3 H, s, CMe), 2.44 (3 H, s, Ar-Me), 3.68 and 3.71 (9 H, 2 s, 3 × OMe), 3.64–3.80 (4 H, partially obscured multiplets, 2 × OCH_2), 5.41 (1 H, s, Ar-C*H*O), 6.53 (1 H, s, Ar-H), 7.27 (4 H, obscured multiplet, 2 × Ar-H of tosyl and 2 × Ar-H of the acetal-substituted ring), 7.50 (2 H, d, *J* 8, 2 × Ar-H), 7.84 (2 H, d, *J* 8, 2 × Ar-H) and 9.20 (1 H, s, NH). Irradiation of the doublet at 7.84 simplified

the obscured multiplet at 7.27 but did not affect the doublet at 7.80; *m/z* (%) (CI) 528 ($M^+ + 1$, 100) and 372 (60) (Found: M^+, 528.2056. $C_{28}H_{34}NO_7S$ requires *M*, 528.205 35).

3,5-*Dimethoxyacetanilide*. 3,5-Dimethoxyaniline (10 g, 0.06 mol) was carefully added to a mixture of glacial acetic acid (6.8 g) and acetic anhydride (6.8 g) with zinc dust (30 mg). The mixture was refluxed for 0.5 h. The hot solution was then poured into water (250 cm^3) with vigorous stirring to give a pale yellow solid. This was collected, washed with water (200 cm^3) and air dried. The crude material was recrystallised from ethyl acetate to give the pure anilide as a colourless crystalline solid (10.2 g, 80%), m.p. 152–153 °C (lit.,[24] 155–156 °C).

Goldberg Reactions.—(b) *Acetanilides*. Copper bronze was activated by treating with a 2% (w/v) solution of iodine in acetone and stirring for 15 min. Filtration was followed by washing with acetone before drying under vacuum. K_2CO_3 was dried at 130 °C overnight. Copper(I) oxide and copper(I) bromide were used without further purification.

Coupling of 3,5-*dimethoxyacetanilide with nitrile* **19** *using copper bronze*. The anilide (2 g, 0.01 mol) and bromo nitrile **19** (2 g, 0.01 mol) were melted together in an atmosphere of nitrogen. Copper bronze (2 g) and potassium carbonate (2 g) were added and the mixture heated at 160–170 °C for 10.5 h. After cooling the mixture was extracted with dichloromethane (8 × 100 cm^3). The combined extracts were washed with water (500 cm^3), dried (Na_2SO_4) and the solvent removed to give a viscous brown oil (3.6 g). Flash chromatography, eluting with increasing concentrations of light petroleum–ethyl acetate then ethyl acetate–methanol yielded three major fractions. Fractions A and B were mixtures and were combined before being re-chromatographed. Fraction C was identified as unchanged anilide (1 g). Careful chromatography, eluting with increasing concentrations of ether in light petroleum yielded three major products. First eluted was unchanged nitrile **19** (53 mg), followed by a yellow crystalline solid (151.6 mg, 6%), m.p. 137–145 °C. Recrystallisation from light petroleum–ether gave pure 4-cyano-N-(3′,5′-*dimethoxyphenyl*)-2-*methylaniline* **5a** as yellow needles, m.p. 148–149 °C; δ_H 2.26 (3 H, s, 3-CH_3), 4.08 (6 H, s, 2 × OCH_3), 5.70 (1 H, s, br, NH), 6.24 (1 H, t, *J* 2, 4′-H), 6.30 (2 H, d, *J* 2, 2′- and 6′-H), 7.24 (1 H, d, *J* 8, 6-H), 7.38 (1 H, d, *J* 8, 5-H) and 7.43 (1 H, s, 3-H); λ_{max}(MeOH)/nm 210 (ε/dm^3 mol^{-1} cm^{-1} 97 500) and 314 (72 500); ν_{max}/cm^{-1} 3300, 2250 and 1600; *m/z* (%) (EI) 269 (M^+, 100), 253 (37) and 237 (24) (Found: C, 71.6; 6.05. $C_{16}H_{16}N_2O_2$ requires C, 71.6; H, 6.03; N, 10.5%). Finally a colourless crystalline solid (26 mg, 1%) was isolated, identified as 4-*bromo*-3-*methyl*-N-(2-*methyl*-4-*cyanophenyl*)*benzamide* **20**, m.p. 180 °C; δ_H 2.40 (3 H, s, 2′-CH_3), 2.52 (3 H, s, 3-CH_3), 7.50–7.78 (6 H, complex m, 2-, 5-, 3′-, 5′-, 6′-H and NH) and 8.54 (1 H, d, *J* 8, 6-H); λ_{max}(MeOH)/nm 219 (ε/dm^3 mol^{-1} cm^{-1} 42 850) and 260 (78 570); ν_{max}(Nujol)/cm^{-1} 3300, 2230 and 1650; *m/z* (%) (EI) 330 (M^+, 17), 328 (15), 197 (100) (F.D.), 327 and 329 (Found: C, 58.6; H, 4.33; N, 8.45%; M^+, 328.027. $C_{16}H_{13}BrN_2O$ requires C, 58.4; H, 3.98; N, 8.51%; *M*, 328.021). By variation of the conditions the yield of the amide **20** was reduced.

Synthesis of the amide **20** *from the bromo nitrile* **19**. The bromonitrile **19** (900 mg, 4.6 mmol) was heated with activated copper (1 g) and potassium carbonate (1 g) at 150 °C in an atmosphere of nitrogen for 10 h. After cooling, the copper residues were extracted with dichloromethane (5 × 20 cm^3). Removal of solvent gave a brown oily solid (600 mg) which on chromatography gave the crude amide **20** as a tan coloured solid (300 mg). Recrystallisation from ether–light petroleum gave the pure amide **20** as needles, m.p. 180 °C. (ν_{max}/cm^{-1} 1650) its other spectral properties were identical to those described above. Concentration of the mother liquors gave a tan coloured solid (12 mg), m.p. 136–137 °C; ν_{max}/cm^{-1} 1680 identified as a rotamer of **20**.

Hydrolysis of amide **20**. The amide **20** (163.3 mg, 0.5 mmol) was dissolved in ethanolic potassium hydroxide (400 mg, 7 mmol, in 8 cm^3) and heated to 70 °C (bath temperature) with stirring for 4.5 h then at 80 °C for a further 3 h before cooling. The mixture was then poured into water (50 cm^3) and the basic solution extracted with ethyl acetate (2 × 50 cm^3). The combined organic layers were washed with water (100 cm^3), dried (Na_2SO_4) and evaporated to dryness to give the crude amine **21** as an off-white solid (69 mg), m.p. 87–93 °C. Recrystallisation from ether–light petroleum gave the pure 4-*cyano*-2-*methylaniline* **21** as colourless crystals, m.p. 90–93 °C (lit.,[16] 94–95 °C); δ_H 2.16 (3 H, s, 2-CH_3), 4.08 (2 H, s, br, NH_2), 6.62 (1 H, d, *J* 8, 6-H) and 7.26 (2 H, d, *J* 8, 3- and 5-H). Acidification of the aqueous solution precipitated a white solid. This was extracted into chloroform (3 × 50 cm^3) and the combined organic layers dried (Na_2SO_4). Removal of the solvent gave the pure 4-*bromo*-3-*methylbenzoic acid* **22** as colourless needles (67.1 mg, 63%), m.p. 204–205 °C (lit.,[17] 209–210 °C); mixed m.p. 202–207 °C; δ_H 2.36 (3 H, s, 3-CH_3), 7.53 (1 H, d, *J* 6, 5-H), 7.73 (1 H, d, *J* 6, 6-H) and 7.86 (1 H, s, 2-H). Spectral data were identical for samples prepared as described in the literature for **21** and from a commercial sample of **22**.

4-*Cyano*-N-(3′,5′-*dimethoxyphenyl*)-2-*methylacetanilide* **10a**. 3,5-Dimethoxyacetanilide (3 g, 0.015 mol) and nitrile **19** (1.5 g, 7.7 mmol) were melted together under an atmosphere of N_2 and treated with copper(I) oxide (2.4 g, 0.017 mol) and potassium carbonate (1.5 g, 0.011 mol). The mixture was maintained at 190–200 °C for 7 h. Work-up *via* ethyl acetate gave a brown solid (4 g). Chromatography (ethyl acetate–light petroleum) gave the *diphenylamine* **5a** (81.5 mg, 2%) and a pale brown oil (1.7 g, 72%) identified by EI mass spectrometry as the amide **10a**. A sample was crystallised from ether to give an off white solid, m.p. 134–138 °C. Recrystallisation from ether–light petroleum gave the pure *diphenylamide* **10a** as a white crystalline solid, m.p. 136–137 °C; ν_{max}(Nujol)/cm^{-1} 2220 (CN) and 1680 (C=O amide); λ_{max} 250/nm (ε/dm^3 mol^{-1} cm^{-1} 21 600) and 208 (63 300). The ^1H NMR spectrum gave only broad peaks. Heating to 100 °C failed to sharpen the peaks; *m/z* (%) 310 (M^+, 67), 268 (98), 253 (50) and 237 (31) (Found: C, 70.0; H, 6.1; N, 9.02%; M^+, 310.1306. $C_{18}H_{18}N_2O_3$ requires C, 69.6; H, 5.90; N, 9.03%; *M*, 310.1317).

Hydrolysis of diphenylamide **10a**. The diphenylamide **10a** (1.5 g, 4.8 mmol) was heated to 60–70 °C (bath temperature) in ethanol (70 cm^3) containing potassium hydroxide (3.95 g, 0.7 mol) with stirring for 1 h. Normal work-up gave the *diphenylamine* **5a** as yellow crystals (1.2 g, 95%); m.p. 138–142 °C. All spectral data were in agreement with that already recorded. This product was normally used without further purification.

4-*Bromo*-N-(3,5-*dimethoxyphenyl*)-3-*methylcinnamamide* **24**. The bromobenzaldehyde **23** (1 g, 7 mmol) and 3,5-dimethoxyacetanilide (1.4 g, 7 mmol) were heated under an atmosphere of N_2 with copper(I) oxide (2.2 g) and potassium carbonate (1.4 g) at 180–200 °C for 6 h. Work-up *via* ethyl acetate gave a brown oil (1.5 g). Flash chromatography, eluting with ethyl acetate–light petroleum (3:7) gave the starting aldehyde **23** (233.2 mg), an orange foam (246.5 mg, 53%) and starting anilide (500 mg). The orange foam was crystallised from ether–light petroleum to yield a colourless crystalline solid, identified as 4-*bromo*-N-(3,5-*dimethoxyphenyl*)-3-*methylcinnamamide* **24**, m.p. 129–130 °C; δ_H 2.40 (3 H, s, CH_3), 3.77 (6 H, s, 2 × OCH_3), 6.26 (1 H, t, *J* 2, 4′-H), 6.53 (1 H, d, *J* 14, *trans* CH=C*H*CO), 6.90 (2 H, s br, 2′ + 6′-H), 7.17 (1 H, dd, *J* 6, 2, 6-H), 7.33 (1 H, d, *J* 2, 2-H), 7.51 (1 H, d, *J* 6, 5-H), 7.56 (1 H, s br, NH) and 7.66 (1 H, d, *J* 14, *trans* C*H*=CHCO); λ_{max}(MeOH)/nm 301 (ε/dm^3 mol^{-1} cm^{-1} 3200); ν_{max}(Nujol)/cm^{-1} 3300, 1680, 1630 and 1600; *m/z* (EI) (%) 377 (M^+, 16) and 375 (M^+, 16) (Found: C, 57.4; H, 4.88; N, 3.58. $C_{18}H_{18}BrNO_3$ requires C, 57.5; H, 4.79; N, 3.72%).

2-(4′-*Bromo*-3′-*methylphenyl*)-5,5-*dimethyl*-1,3-*dioxane* **25**. 4-Bromo-3-methylbenzaldehyde[15b] (1 g, 5 mmol) and 2,2-dimethylpropane-1,3-diol (0.8 g, 9.1 mmol) were heated at reflux in dry toluene (60 cm^3) containing toluene-*p*-sulfonic acid (45 mg) under a Dean and Stark apparatus for 6 h. The mixture was allowed to stand overnight before being basified to pH 9 with ethanolic potassium hydroxide. The mixture was washed with water (150 cm^3) and dried (K_2CO_3). Removal of the solvent gave the *pure dioxane* **25** as a yellow oil which solidified on standing (1.39 g, 98%), m.p. 53–54 °C. Recrystallisation from pentane failed to sharpen the m.p.; δ_H 0.80 (3 H, s, C-CH_3), 1.26 (3 H, s, C-CH_3), 2.39 (3 H, s, 3′-Me), 3.62 (2 H, d, *J* 14, 2 × CHO), 3.78 (2 H, d, *J* 14, 2 × CHO), 5.32 (1 H, s, Ar-C*H*O), 7.15 (1 H, dd, *J* 8, 2, 6′-H), 7.38 (1 H, d, *J* 2, 2′-H) and 7.52 (1 H, d, *J* 8, 5′-H); *m*/*z* (EI) (%) 285 (M^+, 94), 269 (73), 199 (100), 171 (71) and 115 (74) (Found: C, 54.2; H, 5.95. $C_{13}H_{17}BrO_2$ requires C, 54.5; H, 6.01%).

N-(3′,5′-*Dimethoxyphenyl*)-4-(5,5-*dimethyl*-1,3-*dioxan*-2-*yl*)-2-*methylacetanilide* **26**. 3,5-Dimethoxyacetanilide (0.4 g, 2 mmol) and the dioxane **25** (0.5 g, 1.7 mmol) were melted together in an atmosphere of N_2. Copper bronze (0.5 g) and potassium carbonate (0.5 g) were added and the mixture heated to 185–195 °C for 5.5 h. The slurry was cooled and extracted with ethyl acetate (5 × 20 cm^3). Removal of the solvent gave a brown oil (500 mg) and chromatography (ethyl acetate–light petroleum) (1:4 to 4:1) gave 2 main fractions. Fraction 1 (200 mg) was found to be a complex mixture from which only starting material was isolated. Fraction 2 a viscous gum (246.8 mg, 36%) was identified as the required *diphenylamide* **26**. A small sample was crystallised from ether; m.p. 110–112 °C; δ_H 0.81 (3 H, s, CCH_3), 1.30 (3 H, s, CCH_3), 1.93 (3 H, s, br, CH_3CO), 2.26 (3 H, s, 2-CH_3), 3.67 (2 H, s, 2 × CHO), 3.74 (6 H, s, 2 × OCH_3), 3.78 (2 H, m, 2 × C*H*O), 5.40 (1 H, s, ArC*H*O), 6.27 (1 H, s br, 4′-H), 6.42 (2 H, s br, 2′- and 6′-H), 7.26 (1 H, s br, 3 H), 7.40 (1 H, s br, 5-H) and 7.46 (1 H, s br, 6-H); λ_{max}(MeOH)/nm 222 (ε/dm^3 mol^{-1} cm^{-1} 2400) and 287 (32 500); ν_{max}(Nujol)/cm^{-1} 1680; *m*/*z* (%) (EI) 399 (M^+, 72), 398 (100), 360 (75), 312 (68), 274 (60), 273 (95), 272 (72), 178 (93), 115 (72) and 69 (79) (Found: M^+, 399.2028. $C_{23}H_{24}NO_5$ requires *M*, 399.2045).

Hydrolysis of diphenylamide **26**. The diphenylamide **26** (240 mg, 0.60 mmol) was stirred at room temperature in a solution of potassium hydroxide (600 mg, 0.01 mol) in ethanol (10 cm^3) for 1 h. After 2 h at 70–80 °C normal work-up gave an orange oil, which was identified as N-(3′,5′-*dimethoxyphenyl*)-4-(5,5-*dimethyl*-1,3-*dioxan*-2-*yl*-2-*methylaniline* **27** (129.1 mg, 65%); δ_H 0.90 (3 H, s, C-CH_3), 1.51 (3 H, s, C-CH_3), 2.29 (3 H, s, 2-CH_3), 3.64 (2 H, m, CH_2O), 3.74 (6 H, s, 2 × OCH_3), 3.78 (2 H, m, CH_2O), 5.34 (1 H, s, ArC*H*O), 5.40 (1 H, s br, NH), 6.03 (1 H, t, *J* 2, 4′-H), 6.13 (2 H, d, *J* 2, 2′-and 6′-H), 7.26 (2 H, m, 5-and 6-H) and 7.33 (1 H, s, 3-H); λ_{max}(MeOH)/nm 216 (ε/dm^3 mol^{-1} cm^{-1} 23 000), 238 (12 700) and 288 (12 800); ν_{max}(Nujol)/cm^{-1} 1600 and 1520; *m*/*z* (%) (EI) 358 (M^+ + 1, 90), 357 (M^+, 25), 271 (100) and 195 (20) (Found: M^+, 357.1908. $C_{12}H_{27}NO_4$ requires *M*, 357.1939).

4-*Formyl*-N-(3′,5′-*dimethoxyphenyl*)-2-*methylaniline* **28** *from the dioxane* **27**. The diphenylamine **27** (379.5 mg, 1.1 mmol) was stirred in dioxane (30 cm^3) containing HCl (2 mol dm^{-3}; 20 cm^3) at room temperature for 45 min. Normal work-up gave an orange oil. Flash chromatography and elution with ether–light petroleum (1:1) gave the crude *formyldiphenylamine* **28** (147.6 mg, 49%), m.p. 99–104 °C. Recrystallisation from ether–light petroleum gave a yellow microcrystalline solid, m.p. 109.5 °C; δ_H 2.34 (3 H, s, 2-CH_3), 3.81 (6 H, s, 2 × OCH_3), 5.62 (1 H, s, br, NH), 6.25 (1 H, s, 4′-H), 6.36 (2 H, d, *J* 2, 2′- and 6′-H), 7.31 (1 H, d, *J* 6, 6-H), 7.61 (1 H, d, *J* 6, 5-H), 7.78 (1 H, s, 3-H), 9.80 (1 H, s, CHO); λ_{max}(MeOH)/nm 220 (ε/dm^3 mol^{-1} cm^{-1} 60 000) 245 (35 770) and 345 (72 300); ν_{max}(Nujol)/cm^{-1} 3440, 1670, 1600 and 1520; *m*/*z* (%) (EI) 272 (M + 1, 54) and 271 (M^+, 100) (Found: C, 71.0; H, 6.55: N, 5.19%; M^+, 271.1192. $C_{16}H_{17}NO_3$ requires C, 70.8; H, 6.32; N, 5.16%; *M*, 271.1208).

Reduction of the Cyanodiphenylamine **5a**.—Cyanodiphenylamine **5a** (320 mg, 1.19 mmol) in dry toluene (10 cm^3) containing dry dichloromethane (2 cm^3) under an atmosphere of N_2 was cooled to −78 °C and diisobutylaluminium hydride (DIBAL) (1.2 cm^3, 1.5 mol dm^{-3} in toluene, 1.7 mmol) was added dropwise. The mixture was stirred at −78 °C for 0.5 h and then allowed to warm to room temperature over 2 h. Methanol (2 cm^3) was added, followed by 2 mol dm^{-3} HCl (2 cm^3). Work-up with chloroform (5 × 10 cm^3) gave a dark orange solid (253.2 mg, 79%), m.p. 103–107 °C. Recrystallisation from ether–light petroleum gave yellow microcrystals identified as the *formyl diphenylamine* **28**, m.p. 109–110 °C, identical spectroscopically to the material prepared previously; mixed m.p. 108–110 °C.

For the following Goldberg coupling reactions, the potassium carbonate was dried at 180 °C for 24 h prior to its use.

Coupling of acetanilide with 4-*bromo*-3-*methylbenzonitrile* **19**. (*a*) *Using activated copper bronze*. Acetanilide (1.4 g, 10.4 mmol) and nitrile **19** (1.0 g, 5.1 mmol) were melted together in a dry nitrogen atmosphere. Copper bronze (1.5 g) and potassium carbonate (1.25 g) were added to the melt, and the mixture heated to 200–210 °C for 27 h. Extraction with ethyl acetate yielded a brown solid (1.34 g) which on flash chromatography and elution with ethyl acetate–light petroleum (30–70% ethyl acetate) gave three major products. The first was identified as 4-*cyano*-2-*methyl*-N-*phenylaniline* **5b**, obtained as yellow crystals (114.2 mg, 9.5%), m.p. 110–112 °C. Recrystallisation from ethyl acetate–light petroleum gave an analytically pure sample, m.p. 112–113 °C; δ_H 2.28 (3 H, s, 2-Me), 5.76 (1 H, s br, NH) and 7.06–7.44 (8 H, complex m, 8 × ArH); λ_{max}(MeOH)/nm 222 (ε/dm^3 mol^{-1} cm^{-1} 2142) and 309 (3938); *m*/*z* (%) (EI) 209 (M + 1, 15), 208 (M^+, 86), 207 (100), 192 (42), 131 (28) and 102 (21) (Found: C, 80.7; H, 5.65; N, 13.5. $C_{14}H_{12}N_2$ requires C, 80.7; H, 5.81; N, 13.4%). The second product was 4-*cyano*-2-*methyl*-N-*phenylacetanilide* **10b**; isolated as a yellow gummy, solid (190 mg, 15%). The ^1H NMR spectrum gave only very broad signals; λ_{max}(MeOH)/nm 221sh (ε/dm^3 mol^{-1} cm^{-1} 3890); ν_{max}/ cm^{-1} 2215 and 1675; *m*/*z* (%) (EI) 250 (M^+, 5), 208 (90), 207 (100) and 192 (18) (Found: C, 76.6; H, 5.75; N, 11.1. $C_{16}H_{14}N_2O$ requires C, 76.8; H, 5.64; N, 11.2%). Unchanged acetanilide (509 mg) was also isolated from the column.

(*b*) *Using copper*(I) *oxide*. Acetanilide (2.0 g, 14.81 mmol) and the nitrile **19** (1.5 g, 7.65 mmol) were melted together in a dry nitrogen atmosphere. Copper(I) oxide (2.3 g) and potassium carbonate (1.8 g) were added and the mixture heated to 190–200 °C for 18 h. Work-up *via* ethyl acetate gave a brown gummy solid (3.23 g). Chromatography (ethyl acetate–light petroleum) (30–70% ethyl acetate) gave three major components. (1) An orange solid (76 mg), identified as the starting nitrile **19**, (2) a yellow gum (382 mg, 20%), identified as the acetanilide **10b**; all spectral data were identical to that described in the previous experiment, and (3) a cream powder (1.06 g), identified as starting acetanilide.

Hydrolysis of 4-*cyano*-2-*methyl*-N-*phenylacetanilide* **10b**. The diphenylamide **10b** (200 mg, 0.8 mmol) was heated at reflux in ethanol (6.5 cm^3) containing potassium hydroxide (0.36 g), for 1 h until no diphenylamide was visible by TLC. Normal work-up gave an orange–yellow solid (163 mg, 98%), m.p. 108–112 °C. This was chromatographed (ethyl acetate–light petroleum, 30:70) to give 4-cyano-2-methyl-*N*-phenylaniline **5b** as yellow crystals (116 mg, 70%), m.p. 112–113 °C. All spectra were the same as described earlier.

Coupling of 4-*methoxyacetanilide with* 4-*bromo*-3-*methylbenzonitrile* **19** *using copper bronze*. 4-Methoxyacetanilide (2 g, 12 mmol) and the benzonitrile **19** (1.2 g, 6.12 mmol) were melted

together in a dry nitrogen atmosphere. Copper bronze (1.4 g) and potassium carbonate (1.2 g) were added to the melt and heated at 200 °C for 22 h. Work-up with ethyl acetate gave a brown gum (2.62 g). Careful chromatography on silica and elution with 30–50% ethyl acetate in light petroleum gave four major fractions. First eluted was unchanged bromobenzonitrile **19** (56 mg) as a yellow solid, followed by 4-*cyano*-N-(4′-*methoxyphenyl*)-2-*methylaniline* **5c** (131.5 mg, 9%), m.p. 121–124 °C, as a yellow crystalline solid. Recrystallisation from ethyl acetate–light petroleum yielded an analytically pure sample, m.p. 125–127 °C, as pale yellow crystals; δ_H 2.27 (3 H, s, 2-Me), 3.84 (3 H, s, OMe), 5.62 (1 H, s, NH), 6.82 (1 H, d, *J* 8, 6-H), 6.92 (2 H, d, *J* 8, 3′- and 5′-H), 7.12 (2 H, d, *J* 8, 2′- and 6′-H), 7.30 (1 H, d, *J* 8, 5-H) and 7.36 (1 H, s, 3-H); λ_{max}(MeOH)/nm 222sh (ε/dm^3 mol^{-1} cm^{-1} 30 130) and 303 (48 400); ν_{max}/cm^{-1} 3370, 2230 and 1600; *m*/*z* (%) (EI) 238 (M$^+$, 80) and 224 (100) (Found C, 75.8; H, 6.1; N, 11.5. $C_{15}H_{14}N_2O$ requires C, 75.6; H, 5.92; N, 11.8%).

Next eluted was a deep red gummy solid (626.3 mg, 36%) identified as 4-*cyano*-N-(4′-*methoxyphenyl*)-2-*methylacetanilide* **10c**. Attempts to crystallise the gum failed. It showed δ_H 2.14 (3 H, s, 2-Me), 2.38 (3 H, s, NH COMe), 3.82 (3 H, s, OMe), 6.84 (1 H, d, *J* 8, 6-H), 6.90 (2 H, d, *J* 8, 3′- and 5′-H), 7.16 (2 H, m, 2′- and 6′-H), 7.44 (1 H, d, *J* 8, 5-H) and 7.56 (1 H, s, 3-H). Additional signals were observed at δ 3.76, 2.28 and 2.06. On heating the samples in [$^2H_6$]-DMSO at 75 °C these signals reduced in intensity by ≈35%, indicating that they arose from hindered rotation about the amide bond; λ_{max}(MeOH)/nm 232 (ε/dm^3 mol^{-1} cm^{-1} 61 470) and 280sh (28 570); ν_{max}/cm^{-1} 3300, 2215 and 1650; *m*/*z* (%) (EI) 280 (M$^+$, 7), 235 (6), 223 (100) and 205 (22) (Found: C, 72.7; H, 5.8; N, 9.75. $C_{17}H_{16}N_2O$ requires C, 72.8; H, 5.75; N, 9.99%). The final fraction eluted was the unchanged acetanilide as cream crystals (922 mg).

Hydrolysis of 4-*cyano*-N-(4′-*methoxyphenyl*)-2-*methylacetanilide* **10c**. The cyanodiphenylamide **10c** (779 mg) was dissolved in ethanol (35 cm^3) containing potassium hydroxide (1.8 g) and heated to 60–70 °C for 1 h when TLC showed no starting material. Normal work-up yielded yellow crystals identified as 4-cyano-*N*-(4′-methoxyphenyl)-2-methylaniline **5c** (565 mg, 86%), m.p. 121–125 °C. All spectra were identical to those reported earlier.

Coupling of 3,4,5-*trimethoxyacetanilide with* 4-*bromo*-3-*methylbenzonitrile* **19** *using copper*(I) *oxide*. 3,4,5-Trimethoxyacetanilide (1.87 g, 10 mmol) and 4-bromo-3-methylbenzonitrile (1 g, 5.1 mmol) were melted together in a dry argon atmosphere. Cu_2O (1.1 g) and potassium carbonate (1 g) were added to the melt and heated to 190–200 °C for 7.5 h. Work-up *via* ethyl acetate gave a brown solid (2.15 g) which on chromatography and elution with ethyl acetate (30–70% in light petroleum) gave four components. The first [at R_f 0.86 (ethyl acetate–light petroleum, 1:1)] gave pale yellow crystals (34 mg) of the starting nitrile. The product at R_f 0.47, obtained as yellow crystals (73 mg, 5%), was identified as 4-*cyano*-N-(3′,4′,5′-*trimethoxyphenyl*)-2-*methylaniline* **5d**. Recrystallisation of a small portion from ether–light petroleum gave an analytically pure sample, m.p. 145–147 °C; δ_H 2.28 (3 H, s, 2-Me), 3.84 (6 H, s, 2 × OMe), 3.92 (3 H, s, OMe), 5.65 (1 H, s br, NH), 6.40 (2 H, s, 2′- and 6′-H), 7.06 (1 H, d, *J* 8, 6-H), 7.36 (1 H, d, *J* 8, 5-H) and 7.41 (1 H, s, 3-H); λ_{max}(MeOH)/nm 311 (ε/dm^3 mol^{-1} cm^{-1} 19 220); *m*/*z* (%) (EI) 298 (M$^+$, 49), 283 (100) and 255 (20) (Found: M$^+$, 298.1317. $C_{17}H_{18}N_2O_3$ requires *M*, 298.1317). A product at R_f 0.26 was isolated as an off-white solid (364 mg, 21%). Recrystallisation from ethyl acetate–light petroleum gave colourless crystals, of 4-*cyano*-N-(3′,4′,5′-*trimethoxyphenyl*)-2-*methylacetanilide* **10d**; m.p. 139–140 °C; δ_H 2.16 (3 H, s br, 2-Me), 2.34 (3 H, s br, NCOMe), 3.82 (9 H, s br, 3 × OMe), 6.40 (2 H, s, 2′- and 6′-H), 7.22 (1 H, s br, 6-H), 7.45 (1 H, d br, 5-H) and 7.60 (1 H, s br, 3-H); λ_{max}(MeOH)/nm 219 (ε/dm^3 mol^{-1} cm^{-1} 29 940) and 248 (16 390); *m*/*z* (%) (EI) 340 (M$^+$, 49), 298 (15), 283 (100) and 157 (23) (Found: C, 67.0; H, 6.03; N, 8.31. $C_{19}H_{20}N_2O_4$ requires C, 67.05; H, 5.92; N, 8.23%). Later fractions contained the starting anilide and mixtures of this and the diphenylamide **10d**.

Hydrolysis of 4-*cyano*-N-(3′,4′,5′-*trimethoxyphenyl*)-2-*methylacetanilide* **10d**. The diphenylamide **10d** (300 mg, 0.87 mmol) in ethanol (15 cm^3) containing potassium hydroxide (0.78 g) was heated to 50–60 °C for 1 h. Normal work-up gave an orange gum (86 mg, 99%) which was chromatographed and elution with dichloromethane gave 4-cyano-*N*-(3′,4′,5′-trimethoxyphenyl)-2-methylaniline **5d** (as pale yellow crystals (216 mg, 83%). All spectroscopic data were the same as described earlier.

Coupling between 3,4-*methylenedioxyacetanilide* **8e** *and* 4-*bromo*-3-*methylbenzonitrile* **19** *using activated copper bronze*. The anilide **8e** (1 g, 5.6 mmol) and benzonitrile **19** (0.55 g, 2.8 mmol) were melted together under a dry nitrogen atmosphere. Copper bronze (0.6 g) and potassium carbonate (0.5 g) were added and the mixture heated to 190–200 °C for 12 h. Work-up with ethyl acetate gave a crude brown solid (1.3 g), which was submitted to flash chromatography. Elution with 10–30% of ethyl acetate–light petroleum gave five components. The first isolated, R_f 0.81 was a yellow oil (22.1 mg) identified as starting nitrile. The second was a yellow solid, identified as 4-*cyano*-N-(3′,4′-*methylenedioxyphenyl*)-2-*methylaniline* **5e** (5.3 mg, <1%); m.p. 127–130 °C; δ_H 2.25 (3 H, s, 2-Me), 5.58 (1 H, s br, NH), 6.0 (2 H, s, OCH_2O), 6.63 (1 H, d, *J* 8, 6′-H), 6.70 (1 H, d, *J* 2, 2′-H), 6.81 (1 H, d, *J* 8, 5′-H), 6.88 (1 H, d, *J* 8, 6-H), 7.33 (1 H, d, *J* 8, 5-H) and 7.38 (1 H, s, 3-H); λ_{max}(MeOH)/nm 302 (ε/dm^3 mol^{-1} cm^{-1} 5741); *m*/*z* (%) (EI) 252 (M$^+$, 100), 193 (22) and 122 (9) (Found: M$^+$, 252.0899. $C_{15}H_{12}N_2O_2$ requires *M*, 252.0899).

The next product was a brown solid (12.4 mg), m.p. 88–91 °C (lit.,[19] m.p. 94–95 °C) identified as 4-cyano-2-methylaniline; δ_H 2.14 (3 H, s, 2-Me), 4.09 (2 H, s br, NH_2), 6.65 (1 H, d, *J* 8, 6-H) and 7.30 (2 H, m, 3- and 5-H); *m*/*z* (%) (EI) 132 (M$^+$, 100), 131 (93), 104 (15) and 77 (14).

The main product isolated (R_f 0.15) was a pale brown, gummy solid (107.5 mg, 13%) identified as 4-*cyano*-N-(3′,4′-*methylenedioxyphenyl*)-2-*methylacetanilide* **10e**; δ_H 2.14 (3 H, s, 2-Me), 2.32 (3 H, s, NCOMe), 6.00 (2 H, s, OCH_2O), 6.70 (1 H, d, *J* 8, 6′-H), 6.72 (1 H, d, *J* 2, 2′-H), 6.80 (1 H, d, *J* 8, 5′-H), 7.18 (1 H, d, *J* 8, 6-H), 7.46 (1 H, d, *J* 8, 5-H) and 7.56 (1 H, s, 3-H). A further set of signals of lower intensity were observed at δ 1.92, 2.24, 5.90, 6.54, 7.39 and 7.60. These were unchanged on heating the sample in [$^2H_6$]DMSO at 100 °C and were assigned to a rotamer of the main product; *m*/*z* (%) (EI) 294 (M$^+$, 41), 252 (100), 193 (15) and 157 (12) (Found: M$^+$, 294.1004. $C_{17}H_{14}N_2O_3$ requires *M*, 294.1004). The final component isolated was the starting anilide **8e** (355 mg).

Hydrolysis of 4-*cyano*-N-(3′,4′-*methylenedioxyphenyl*)-2-*methylacetanilide* **10e**. The diphenylamide **10e** (131 mg, 0.45 mmol) in ethanol (6 cm^3) containing potassium hydroxide (0.34 g) was warmed to 55–60 °C for 2 h. Normal work-up yielded the diphenylamine **5e** as a pale yellow crystalline solid (92.4 mg, 82%), m.p. 128–130 °C. All spectra were the same as previously reported.

Preparation of 3-*cyano*-1-*methylcarbazole* **6a**. The diphenylamine **5b** (97.6 mg, 0.47 mmol) was refluxed in trifluoroacetic acid (TFA) (6 cm^3) containing palladium(II) acetate (117.3 mg, 0.94 mmol) under a nitrogen atmosphere for 2 h. After cooling, the TFA was removed under reduced pressure. The palladium residues were extracted with dichloromethane (5 × 10 cm^3) and filtered. The combined organic filtrates were washed with water (40 cm^3) and dried (Na_2SO_4). Evaporation of the solvent yielded a dark yellow solid (50 mg), which was chromatographed. Elution with ethyl acetate (10–40% in light petroleum) gave the title carbazole **6a** as a white powder (29.4 mg, 30%),

m.p. 195–196 °C (lit.,[18] m.p. 193 °C); δ_H([$^2H_6$]-acetone) 2.64 (3 H, s, 1-Me), 7.28 (1 H, t, *J* 8, 6-H), 7.50 (1 H, t, *J* 8, 7-H), 7.54 (1 H, s, 2-H), 7.60 (1 H, d, *J* 8, 8-H), 8.24 (1 H, d, *J* 8, 5-H), 8.42 (1 H, s, 4-H) and 10.85 (1 H, s br, NH); λ_{max}(MeOH)/nm 233 (ε/dm^3 mol^{-1} cm^{-1} 8725), 242 (8720), 257sh (9850), 272 (12 930), 322 (1130) and 336 (775); *m/z* (%) (EI) 207 (M + 1, 35), 206 (M$^+$, 100), 191 (7), 177 (31), 165 (9) and 103 (67).

3-*Cyano*-6-*methoxy*-1-*methylcarbazole* **6b**. The cyanodiphenylamine **5c** (110 mg, 0.46 mmol) and palladium(II) acetate (212 mg, 0.94 mmol) were refluxed in TFA (6 cm^3) under nitrogen for 2.25 h. The crude product was obtained as above as an orange solid (75 mg). The solid was chromatographed on silica and elution with dichloromethane gave the title *carbazole* **6b** as a white powder (54.8 mg, 50%); m.p. 188–190 °C; ν_{max}/cm^{-1} 3370 (NH), 2230 (CN) and 1610 (CO); δ_H([$^2H_6$]-DMSO) 2.56 (3 H, s, 1-Me), 3.86 (3 H, s, OMe), 7.12 (1 H, dd, *J* 8, 3, 7-H), 7.48 (1 H, d, *J* 8, 8-H), 7.54 (1 H, s, 2-H), 7.82 (1 H, d, *J* 3, 5-H), 8.52 (1 H, s, 4-H) and 11.65 (1 H, s, NH); λ_{max}(MeOH)/nm 222 (ε/dm^3 mol^{-1} cm^{-1} 18 310) 263sh (12 880), 282 (21 460) and 296sh (13 870); ν_{max}(Nujol)/cm^{-1} 3370, 2230 and 1610; *m/z* (%) (EI) 237 (M + 1, 7), 236 (M$^+$, 22), 221 (100), 193 (76) and 164 (34) (Found: M$^+$, 236.0950. $C_{15}H_{12}N_2O$ requires *M*, 236.0950).

3-*Formyl*-6-*methoxy*-1-*methylcarbazole* **30a**. The DIBAL was calibrated immediately prior to use by means of gas titration.

The cyanocarbazole **6b** (104.4 mg, 0.44 mmol) was suspended in diglyme (5.5 cm^3) under a dry nitrogen atmosphere and cooled to −78 °C (bath temperature). DIBAL (1.3 cm^3, 1.3 mmol) was slowly added to the stirring mixture and after 15 min at −78 °C the cooling bath was removed and the reaction allowed to warm to room temperature for 2 h. The reaction mixture was cooled in an ice bath and 2 mol dm^{-3} hydrochloric acid (12 cm^3) was carefully added. The ice bath was removed and the mixture stirred for a further 90 min at room temperature before being treated with water (25 cm^3) and extracted with chloroform (6 × 10 cm^3). The combined organic extracts were washed with water (2 × 10 cm^3) and dried (Na_2SO_4). Solvent removal yielded the crude carbazole **30a** as a yellow-orange solid (50 mg, 48%). Chromatography, eluting with ether–light petroleum (75:25) gave the pure 3-formylcarbazole **30a** as a pale cream powder (38 mg, 36%), m.p. 202–203 °C (lit.,[19] m.p. 191–192 °C); δ_H([$^2H_6$]-acetone) 2.63 (3 H, s, 1-Me), 3.92 (3 H, s, OMe), 7.11 (1 H, dd, *J* 7, 7-H), 7.51 (1 H, d, *J* 7, 8-H), 7.75 (1 H, s, 2-H), 7.83 (1 H, d, *J* 7, 5-H), 8.53 (1 H, s, 4-H), 10.04 (1 H, s, CHO) and 10.66 (1 H, s br, NH); λ_{max}(MeOH)/nm 230 (ε/dm^3 mol^{-1} cm^{-1} 6655) 248 (5700), 280 (6625), 298 (7410) and 335 (2104); ν_{max}(Nujol)/cm^{-1} 3325, 1679 and 1595; *m/z* (%) (EI) 239 (M$^+$, 100), 224 (100), 196 (22) and 167 (10) (Found: M$^+$, 239.0946. Calc. for $C_{15}H_{13}NO_2$: *M*, 239.0946).

3-*Cyano*-5,6,7-*trimethoxy*-1-*methylcarbazole* **6c**. The diphenylamine **5d** (110 mg, 0.37 mmol) and palladium(II) acetate (160 mg, 0.71 mmol) were heated to reflux in acetic acid (6 cm^3) for 1 h in an argon atmosphere. The reaction was cooled and work-up as before left an orange solid (82.5 mg) which was chromatographed eluting with dichloromethane to give the title *carbazole* **6c** as a white powder (62.5 mg, 57%), m.p. 193–196 °C. Rechromatography of a portion of the material gave an analytically pure sample, m.p. 202–203 °C; δ_H 2.54 (3 H, s, 1-Me), 3.92 (3 H, s, OMe), 3.94 (3 H, s, OMe), 4.19 (3 H, s, OMe), 6.75 (1 H, s, 8-H), 7.37 (1 H, m, 2-H), 8.29 (1 H, s br, NH) and 8.34 (1 H, s, 4-H); λ_{max}(MeOH)/nm 238 (ε/dm^3 mol^{-1} cm^{-1} 15 800), 252 (18 950), 275 (20 640) and 318 (4500); *m/z* (%) (EI) 297 (M$^+$ + 1, 19), 296 (M$^+$, 81), 281 (100), 238 (49) and 223 (81) (Found: M$^+$, 296.1161. $C_{17}H_{16}N_2O_3$ requires *M*, 296.1161).

3-*Formyl*-5,6,7-*trimethoxy*-1-*methylcarbazole* **30b**. The DIBAL was calibrated by means of gas titration immediately prior to use.

The cyanocarbazole **6c** (26 mg, 0.0878 mmol) was suspended in diglyme (1 cm^3) under a dry nitrogen atmosphere and cooled to −78 °C (bath temperature). DIBAL (0.25 cm^3, 0.25 mmol) was slowly added to the stirring mixture and after 15 min the cooling bath was removed. The resulting yellow solution was stirred at room temperature for 2 h. The reaction was cooled in an ice bath and 2 mol dm^{-3} hydrochloric acid (2.5 cm^3) was carefully added. The ice bath was removed and the reaction stirred at room temperature for a further 90 min, after which water (5 cm^3) was added and the aqueous mixture worked up *via* chloroform to give the crude formylcarbazole **30b** as a yellow solid (18 mg, 69%). Chromatography (ether–light petroleum, 80:20) gave the 3-*formylcarbazole* **30b**, m.p. 185–187 °C; δ_H 2.58 (3 H, s, 1-Me), 3.91 (3 H, s, OMe), 3.93 (3 H, s, OMe), 4.20 (3 H, s, OMe), 6.80 (1 H, s, 8-H), 7.72 (1 H, s, 2-H), 8.40 (1 H, s br, NH), 8.50 (1 H, s, 4-H) and 10.10 (1 H, s, CHO); λ_{max}(MeOH)/nm 214 (ε/dm^3 mol^{-1} cm^{-1} 3045), 241 (4890), 282 (5515), 293sh (4240) and 329 (1600); ν_{max}($CHCl_3$)/cm^{-1} 3340, 1678 and 1594; *m/z* (%) (EI) 299 (M$^+$, 100), 284 (95), 256 (20), 241 (25), 226 (38) and 149 (30) (Found: M$^+$, 299.1158. $C_{17}H_{17}NO_4$ requires *M*, 299.1157).

Oxidation of 4-*cyano*-N-(3′,4′-*methylenedioxyphenyl*)-2-*methylaniline* **5e**. The diphenylamine **5e** (118.4 mg, 0.4 mmol) was dissolved in acetic acid (18 cm^3) under nitrogen. Palladium(II) acetate (212.5 mg, 0.9 mmol) was added and the mixture heated at reflux for 45 min. After removal of solvent the remaining black solid was thoroughly extracted with boiling dichloromethane (7 × 10 cm^3). The combined organic extracts were washed with dilute aqueous sodium hydrogen carbonate (20 cm^3) and water (20 cm^3) and dried (Na_2SO_4). Solvent evaporation yielded a yellow solid (72.4 mg) which was chromatographed with dichloromethane to give an inseparable mixture of 3-cyano-6,7-(methylenedioxy)-1-methylcarbazole **33** and 3-cyano-5,6-methylenedioxy-1-methylcarbazole **34** in the ratio of 6:1 in favour of the 6,7-isomer, as a fine white powder (45 mg, 45%), m.p. 275–277 °C; λ_{max}/nm 348 (ε/dm^3 mol^{-1} cm^{-1} 1850), 284 (11 900), 251 (8170) and 225 (6900).

The ^{1}H NMR signals of the 6,7-isomer were as follows; δ([$^2H_6$]-acetone) 10.75 (1 H, br s, N-H), 8.28 (1 H, s, 4-H), 7.65 (1 H, s, 5-H), 7.41 (1 H, m, 2-H), 7.05 (1 H, s, 8-H), 6.08 (2 H, s, CH_2) and 2.59 (3 H, s, 1-Me); the signals due to the 5,6-isomer of greatly reduced intensity were at δ 8.14 (1 H, s, 4-H), 7.54 (1 H, m, 2-H), 7.13 (1 H, d, *J* 7, Ar-H), 7.04 (1 H, d, *J* 7, Ar-H), 6.22 (2 H, s, CH_2) and 2.62 (3 H, s, 1-Me). The mixture gave *m/z* (%) 250 (M$^+$, 100), 192 (13) and 125 (18) (Found: M$^+$, 250.0742. $C_{15}H_{10}N_2O_2$ requires *M*, 250.0742).

Oxidation of the cyano diphenylamine **5a** *by palladium*(II) *acetate*. The cyano diphenylamine **5a** (500 mg, 1.8 mmol) and palladium(II) acetate (825.1 mg, 3.7 mmol) were refluxed for 1 h in glacial acetic acid (120 cm^3) under an atmosphere of nitrogen. The mixture was allowed to cool before the acetic acid was removed under reduced pressure. The black residues were extracted with chloroform (2 × 100 cm^3) and gave the crude product as an orange solid (440.3 mg, 89%). Chromatography, and elution with dichloromethane gave 3-*cyano*-5,7-*dimethoxy*-1-*methylcarbazole* **6d** as an amorphous yellow powder (268.9 mg, 55%); m.p. 269–270 °C; δ_H 2.56 (3 H, s, 1-CH_3), 3.96 (3 H, s, 7-OCH_3), 4.02 (3 H, s, 5-OCH_3), 6.36 (1 H, d, *J* 2, 6-H), 6.59 (1 H, d, *J* 2, 8-H), 7.34 (1 H, s, 2-H), 8.19 (1 H, s br, NH) and 8.36 (1 H, s, 4-H); λ_{max}(MeOH)/nm 220 (ε/dm^3 mol^{-1} cm^{-1} 5440), 232 (48 900), 270 (8560), 288sh (5000), 315 (1600) and 328 (1220); ν_{max}/cm^{-1} 3340, 2220 and 1600; *m/z* (%) (EI) 267 (100, M + 1), 252 (10), 24 (40) and 208 (28) (Found: M$^+$, 267.1088. $C_{16}H_{15}N_2O_2$ requires *M*, 267.1133).

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