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# Synthesis of Phenanthridines by Radical $C_{aryl}$-$C_{aryl}$ Coupling

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***Abstract:*** Treatment of N-(*o*-bromobenzyl)anilines with 1-3 equivalent amounts of *n*-tributyltinhydride, in the presence of 0.5 to 0.6 mol equiv. of AIBN, results in the formation of phenanthridines in good yields. The mechanism of the oxidation step is probed with a deuterated aniline derivative and azo*bis*cyclohexylcarbanonitrile (ABCN) as the initiator. It is shown that the carbon centred radical derived from the latter does not act as the hydrogen abstracting species. Copyright © 1996 Elsevier Science Ltd

Carbon radicals, thermally generated from organic halides or chalcogens by the use of stannylhydride and an initiator have proven themselves to be versatile intermediates in organic synthesis.[1] Although the addition of such radicals to a normal olefin lacking any electronic bias in an intermolecular process is considered to be synthetically unattractive, the same is not true for the intramolecular reactions and such processes have been advantageously utilised for the establishment of $C_{aryl}$—$C_{aryl}$ bond.[2] We report here full details pertaining to a practical synthesis[3a,b] of polyalkoxyphenanthridines,[3c,4] and discuss in some detail the mechanistic aspects of the reactions.

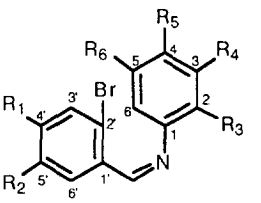
The requisite starting materials for phenanthridines, the N-(*o*-bromobenzylidene)anilines (**1**), are readily obtained as crystalline solids from the corresponding aromatic aldehydes and anilines by condensation of the two components in boiling ethanol. The various Schiff's bases **1** thus prepared are collected in Table 1.

The conversion of these imines into the corresponding secondary amines, namely, the N-(*o*-bromobenzyl)anilines **2**, was achieved by treatment of the former with sodium borohydride ( 3-4 equiv. ) in MeOH at 0°C, and the course of reduction conveniently followed by the disappearance of the yellow colour due to starting materials. The various N-bromobenzyl derivatives **2** thus obtained are collected in Table 2.

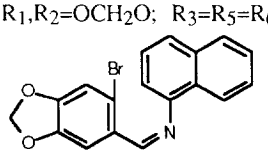
Wherever difficulties were encountered in the preparation of the imines or when the requisite *o*-bromobenzyl halide was available commercially, the alternative method involving mono N-alkylation of the NH compounds was employed. Compounds **2j**-**2n** ( Table 2 ) were secured by this procedure.

When equimolecular quantities of the bromoaniline **2a** and *n*-$Bu_3SnH$ ( TBTH ), in benzene under reflux, was treated with the conventional catalytic quantity of AIBN ( 0.1 equiv. ) to initiate the radical process, the yield

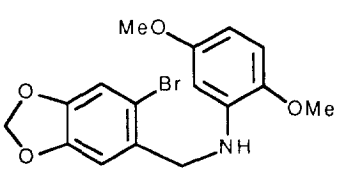
**Table 1**. Benzylideneanilines **1**.



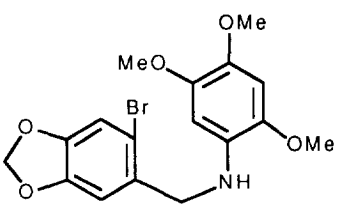
**1**

| | | Yield (%) |
|---|---|---|
| **1a** | $R_1$=$R_2$=OMe; $R_3$=$R_4$=$R_5$=$R_6$=H | 87 |
| **1b** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_4$=$R_5$=$R_6$=H | 74 |
| **1c** | $R_1$,$R_2$=$OCH_2O$; $R_3$=OMe ; $R_4$=$R_5$=$R_6$=H | 90 |
| **1d** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_5$=$R_6$=H ; $R_4$=OMe | 93 |
| **1e** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_4$=$R_6$=H ; $R_5$=OMe | 86 |
| **1f** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_5$=OMe ; $R_4$=$R_6$=H | 90 |
| **1g** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_5$=H ; $R_4$=$R_6$=OMe | 80 |
| **1h** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_5$=$R_6$=OMe ; $R_4$=H | 82 |
| **1i** |  | 89 |

of phenanthridine formed was very low, with most of the starting material remaining unaltered. Progressive increase in the yield of the product was observed with addition of further quantities of AIBN and the total consumption of the bromide observed only when 0.5-0.6 mol. equiv. of the initiator was employed. With the



**2k**

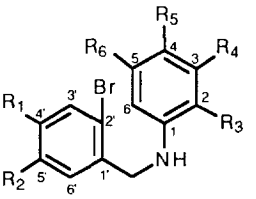


**2h**

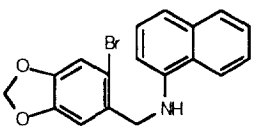
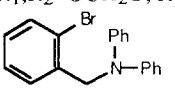
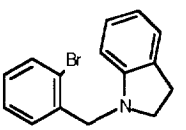
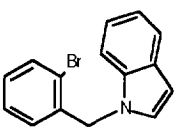
optimum condition thus secured, the study of the chemistry of the radical generated from the bromo compounds **2a-2k** was undertaken. The phenanthridines **3** prepared by the method are collected in Table 3.

It can thus been seen that the reaction constitutes a viable and preparatively useful alternative method[3a] for phenanthridines which are formed in good yields ( Table 3 ) **3a-3k**, including 1-substituted phenanthridines, despite steric crowding around the central biphenyl C-C axis. The relative unimportance of steric factors in radical cyclisation is well-known and the formation of the two isomers **3d** and **3d'** in approximately equal amounts bear witness to this fact. It should also be noted that the benzo(*c*)phenanthridine[5a,b] nucleus **3i** present in many biologically active alkaloids is readily accessible from simple starting materials and in good yield.

**Table 2.** N-Bromobenzylanilines **2.**

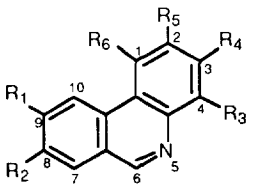


**2**

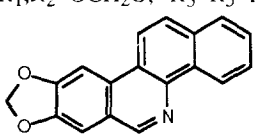
| | | Yield (%) |
|---|---|---|
| **2a** | $R_1$=$R_2$=OMe; $R_3$=$R_4$=$R_5$=$R_6$=H | 48 |
| **2b** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_4$=$R_5$=$R_6$=H | 93 |
| **2c** | $R_1$,$R_2$=$OCH_2O$; $R_3$=OMe ; $R_4$=$R_5$=$R_6$=H | 74 |
| **2d** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_5$=$R_6$=H ; $R_4$=OMe | 81 |
| **2e** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_4$=$R_6$=H ; $R_5$=OMe | 69 |
| **2f** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_5$=OMe ; $R_4$=$R_6$=H | 84 |
| **2g** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_5$=H ; $R_4$=$R_6$=OMe | 65 |
| **2h** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_5$=$R_6$=OMe ; $R_4$=H | 87 |
| **2i** |  | 68 |
| **2j** | $R_1$=$R_2$=$R_3$=$R_6$=H; $R_4$,$R_5$=$OCH_2O$ | 74 |
| **2k** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_6$=OMe ; $R_4$=$R_5$=H | 37 |
| **2l** |  | 21 |
| **2m** |  | 97 |
| **2n** |  | 70 |

It is of interest to note that the N-bromobenzylindole ( **2n** ) on radical generation did not yield the pyrrolophenanthridine ( **4** ) ( *cf.* Scheme 1 ). Instead, and not unexpectedly, the two compounds formed in the reaction were assigned the isoindoloindole structures[6] **5** ( R=H ) and **6** ( R=H ), respectively, on the basis of elemental analyses and NMR spectra.

**Table 3.** Synthesis of Phenanthridines **3**.

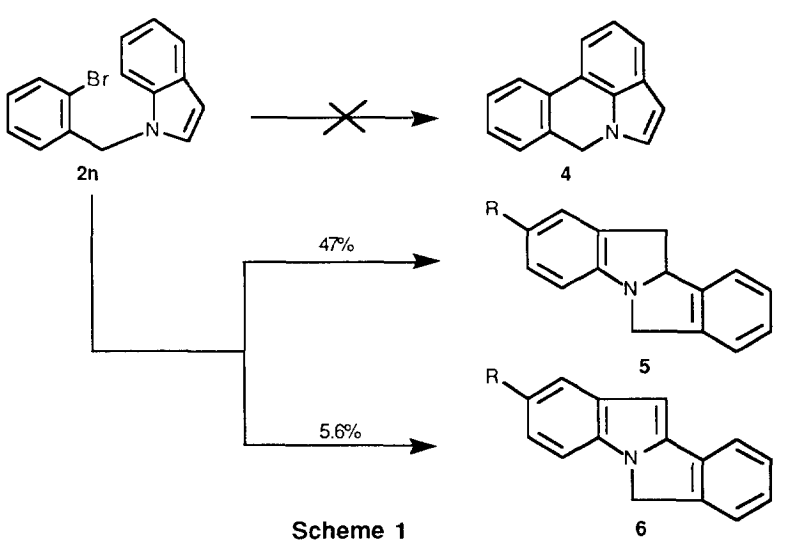


**3**

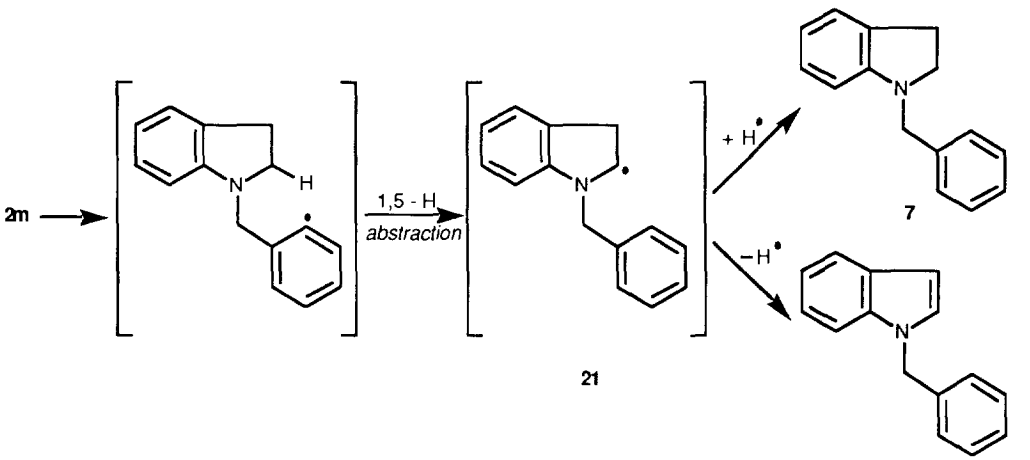
| | | Yield (%) |
|---|---|---|
| **3a** | $R_1$=$R_2$=OMe; $R_3$=$R_4$=$R_5$=$R_6$=H | 68 |
| **3b** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_4$=$R_5$=$R_6$=H | 66 |
| **3c** | $R_1$,$R_2$=$OCH_2O$; $R_3$=OMe ; $R_4$=$R_5$=$R_6$=H | 63 |
| **3d** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_5$=$R_6$=H ; $R_4$=OMe | 34 a) |
| **3d'** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_4$=$R_5$=H ; $R_6$=OMe | 28 a) |
| **3e** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_4$=$R_6$=H ; $R_5$=OMe | 67 |
| **3f** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_5$=OMe ; $R_4$=$R_6$=H | 60 |
| **3g** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_5$=H ; $R_4$=$R_6$=OMe | 62 |
| **3h** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_5$=$R_6$=OMe ; $R_4$=H | 61 |
| **3i** |  | 66 |
| **3j** | $R_1$=$R_2$=$R_3$=$R_6$=H; $R_4$,$R_5$=$OCH_2O$ | 62 |
| **3k** | $R_1$,$R_2$=$OCH_2O$; $R_3$=$R_6$=OMe ; $R_4$=$R_5$=H | 60 |

a) Both compounds obtained from **2d**.

The bromo-dihydroindole ( **2m** ) gave the debromo compound ( **7** ) as the major product ( 74% ), accompanied by small amounts of N-benzylindole ( 5.6% ) (*cf.* Scheme 2).




**Scheme 1**




**Scheme 2**

*On the mechanism of the phenanthridine formation:*

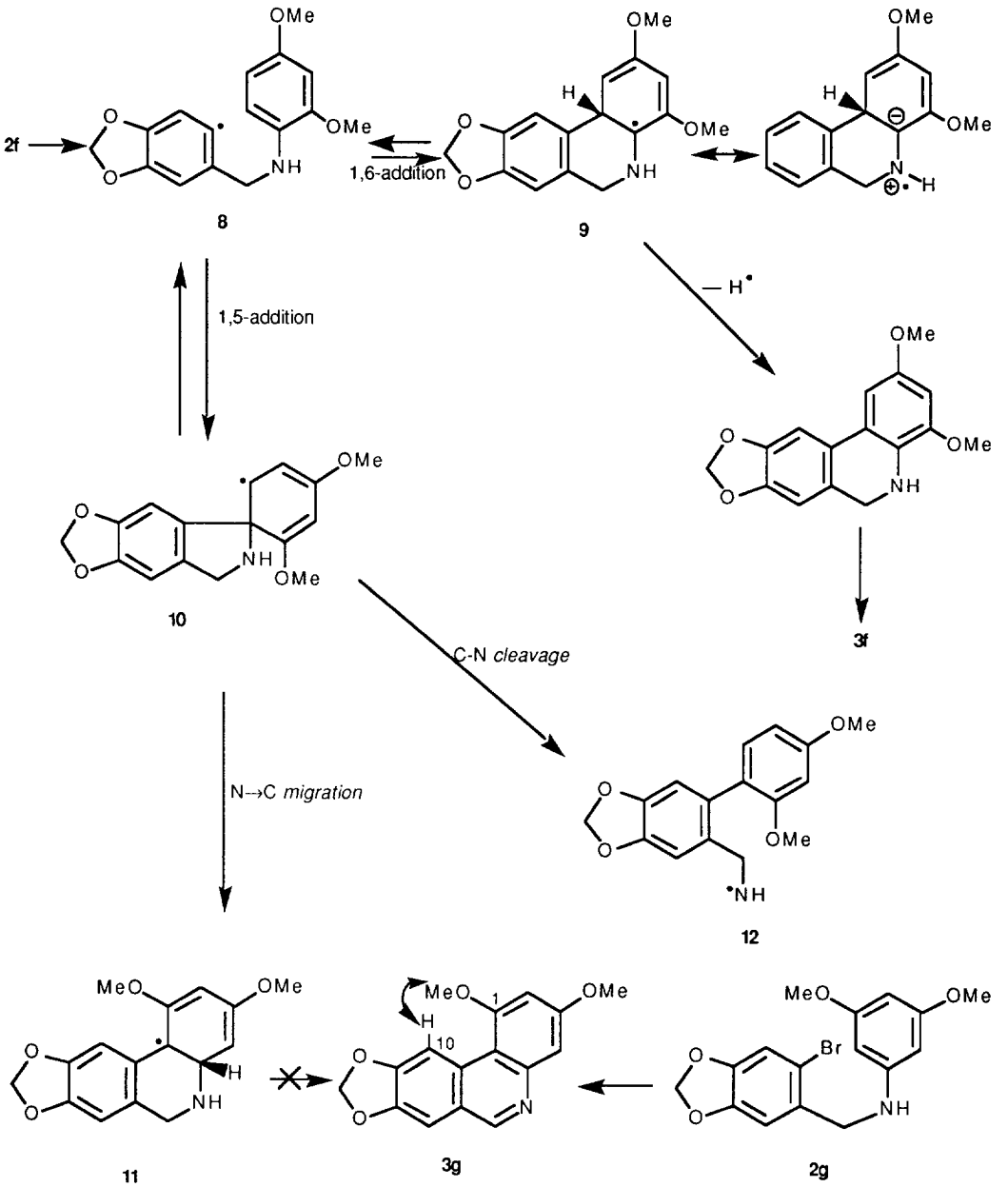
Referring to the chemistry involved in the formation of the phenanthridine **3f**, its genesis can be represented as shown in Scheme 3.

The addition of the thermally generated[7] σ radical **8**, from **2f**, to the neighbouring aromatic ring can operate via a 1,6 addition to give the radical **9** or alternatively via a 1,5 mode to generate the isomeric radical **10**. In the former, the radical is tertiary and derives additional stabilisation[8] from the adjacent nitrogen lone pair. The latter, a kinetically preferred[9] intermediate can, in principle, undergo a C→C migration to generate the species **9**, rearrange with N-translocation[10] to produce a new cyclohexadienyl radical **11** or suffer a C-N cleavage to yield the aminyl radical **12** ( see following paper ).

Both these radicals **9** or **11**, by a formal loss of a H atom, would lead to the dihydrophenanthridine[11] and thence, via aerial oxidation, to the heterocycle. Definitive conclusion as to whether nitrogen migration did indeed occur in the formation of phenanthridines was drawn from the analysis of the NMR spectrum of the product derived from **2f**. It is well known[12] that a methoxy group at C-1 in a phenanthrene molecule causes a pronounced diamagnetic deshielding of the $C_{10}$ hydrogen in the peri position. However, no such low field proton could be discerned in the spectrum of **3f**, the hydrogen in question resonating as a 1H singlet with a normal δ value of 7.61 ppm. On the other hand, the phenanthridine **3g** formed in the reaction of the isomeric N-bromobenzylaniline **2g** did possess one such deshielded proton at δ 8.81 ppm. Similar low field protons were also recorded for products derived from other two *o*-bromobenzylamines **2k** and **2h**, respectively.

This observation therefore provides compelling evidence that the radical **9** is in the reaction pathway leading to the final product, namely, the phenanthridine **3f**. It may stem directly from **8** by a 1,6 addition, or as a consequence of reversibility[13] existing between **8** and **10**.

We amongst others[14] have been intrigued by the occurence of an oxidative process, *viz.* the loss of hydrogen atom from the radical **9** under what are essentially reducing conditions. The fact that, in all these reactions, *1 equiv. of TBTH and 0.5-0.6 mol equiv. of AIBN* were essential to obtain good yields of phenanthridines ( >60% ) led us to suspect that the latter may be acting as more than a mere radical initiator. Turning our attention to radical **9**, the precursor of the dihydrophenanthridine, the aromatisation could take place


2f
8
1,6-addition
9
1,5-addition
— H•
10
3f
C-N cleavage
N→C migration
12
11
3g
2g

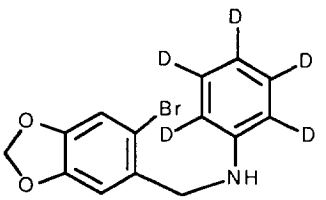
**Scheme 3**

by the loss of a H atom attached either to the carbon atom or to the nitrogen atom. It was therefore of interest to study the chemistry of a molecule lacking the N-H group.

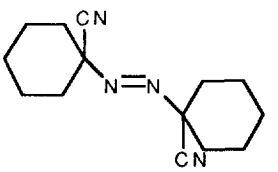
Accordingly N-(*o*-bromobenzyl)-N,N-diphenylamine ( **21** ) was subjected to the action of *n*-$Bu_3SnH$ and AIBN. The product ( mp: 224-226°C ) obtained in 57% yield, was found to have spectra ( IR and $^1H$ NMR ) identical with those of 5-phenyl-6-oxo-5,6-dihydrophenanthridine, ( lit.[15] mp: 225°C ), thus showing that a successful cyclisation does not depend on the presence of the NH group.

*Is the radical* $Me_2(CN)C^{\bullet}$ *the oxidant ?*

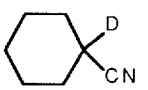
This question was sought to be answered by working with the *o*-bromobenzyl aniline **13**, where the aniline ring is substituted with deuterium, and employing 1,1-azo*bis*cyclohexylcarbonitrile ( ABCN , 0.5-0.6 mol equiv. ) ( **14** ) as the initiator. Formation of the resulting deuterated product **15**, as opposed to **16**, would



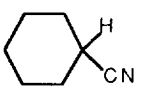

**13**



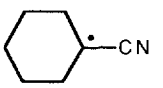

**14**




**15**

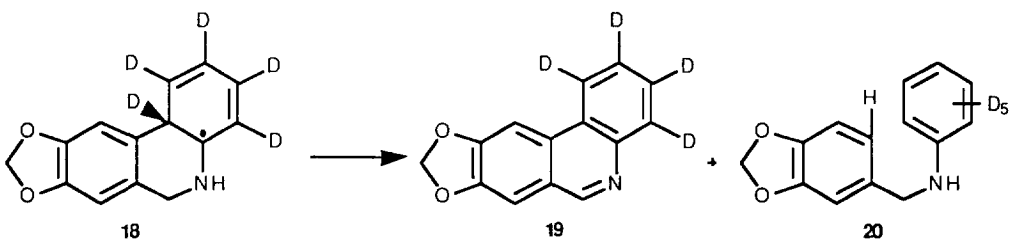



**16**




**17**

be a convincing answer that the radical **17** was abstracting the D atom from the labelled phenantridine radical **18** (Scheme 4). The reaction was performed in degassed toluene ( reflux ; 17 h ) until disappearance of the starting




**18** **19** **20**

**Scheme 4**

material **13**. After careful evaporation of the solvent, the residue was dissolved in $CH_3CN$ to which was added dropwise an ethereal solution of iodine until a faint yellow colour persisted. The mixture was then extracted with *n*-hexane. From the $CH_3CN$-ether solution, 8,9-methylenedioxy-1,2,3,4-tetradeuterophenanthridine **19** ( 66% yield ; $M^+$ 229 ) and the debromo compound **20** ( $M^+$ 232 ) were isolated by chromatography. The *n*-hexane extract was evaporated at atmospheric pressure, the residue redissolved in *n*-pentane and the products therein analysed by GCMS ( Table 4 ). Their mass spectra were then compared with the relevant mass ions obtained from authentic samples of **15** and **16**, obtained respectively from decomposition of ABCN in the presence of *n*-

$Bu_3Sn$-D and *n*-$Bu_3Sn$-H respectively. As can be seen from Table 4, the absence of any peak at m/z 110 ( $M^+$ 110 for $C_7H_{10}ND$, **15** ) indicates that the carbon centered radical **17** is not the oxidising agent and

**Table 4.** Mass Ions Obtained for Cyclohexylcyanide[a].

| Cyclohexylcyanide | m/z 108 (%) | m/z 109 (%) | m/z 110 (%) |
|---|---|---|---|
| **15** | 3.1 ($M^+$-2) | 13.6 ($M^+$-1) | 5.3 ($M^+$) |
| **16** | 13.4 ($M^+$-1) | 5.6 ($M^+$) | 0.9 ($M^+$+1) |
| From reaction **13** + ABCN | 13.4 | 6.7 | — |
| From reaction **2b** + ABCN | 12.6 | 5.4 | — |

a) All ion percentages normalised to parent ion m/z 41.

therefore the isomeric nitrogen radical or neutral molecules, such as AIBN,[14b] could be implicated in such an oxidative process.

Referring to **2n** (Scheme 1) the radical generated from it gives the product of 1,5 addition due to the process being both kinetically and energetically more favourable ( *ie*, not entailing loss of aromaticity of the benzene ring ) and aided probably by the conformational preference of the two benzene rings to stay as far apart as possible.

Finally the reaction of the bromodihydroindole **2m**, which yields two products, N-benzylindole and the dihydro derivative **7**, is best explained on the basis of the new radical **21** formed by a 1,5-H abstraction[16] as the common intermediate (Scheme 2). Thus while quenching of **21** with TBTH leads to **7**, loss of a hydrogen atom provides N-benzylindole.

## CONCLUSION

A preparatively useful intramolecular radical reaction from N-(*o*-bromobenzyl)anilines leading to phenanthridines is described. Their formation occurs by a 1,6 addition to the least substituted carbon *ortho* to the nitrogen atom. It is proposed that, in the series of *o*-bromobenzylanilines studied, the radical addition is fast, the rate determining step being the oxidation to dihydrophenanthridines. And if the spirocyclohexadienyl radical is indeed formed by a 1,5 process, then the absence of any product resulting from β-scission or dimerisation would appear to indicate that *it is in equilibrium with the σ radical.* The reaction as a consequence in channeled through the isomeric cyclohexadienyl radical which undergoes oxidative aromatisation at a rate faster than the aforementioned β-cleavage or dimerisation. The final aromatisation step is shown not to involve the carbon radical derived from the initiator (AIBN) as the hydrogen abstracting species.

## ACKNOWLEDGMENTS

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award of post-graduate fellowships. We are grateful to Professor R. A. Abramovitch for copies of NMR and IR spectra of N-phenylphenantridone. We are indebted to the analytical division, INETI, Queluz, for microanalyses.

## EXPERIMENTAL

*General.* Melting points were determined with a microscopic hot-stage Reichert Thermovar and are uncorrected. Preparative thin layer chromatography ( PTLC ) were performed on plates precoated with silica gel ( 0.5 mm or 2 mm ). Infrared ( IR ) spectra were obtained on potassium bromide discs with a Perkin-Elmer 157G and 683 grating infrared spectrophotometer and the frequencies reported in $cm^{-1}$. Proton nuclear magnetic resonance spectra ( $^1H$ NMR ) were obtained at 300 MHz with a Brücker CXP 380 or General Electric GE-NMR and those at 60 MHz with a Perkin Elmer R 12 B instrument. Chemical shifts are reported in ppm down field from tetramethylsilane and $CDCl_3$ used as solvent unless stated otherwise. High and low resolution mass spectra ( HREIMS and EIMS ) were measured in a Kratos MS-25RF instrument using electron impact at 70 e V. All solvents were purified by standard methods.

**General procedure[17] for the Preparation of the Schiff's bases, the *o*-Bromobenzylidene anilines.** The appropriate *o*-bromobenzaldehyde ( 0.02 mol ) and the aniline ( 0.03 mol ) in anhydrous EtOH ( 5 ml ) were heated under reflux ( 15 min ). The yellow solid that precipitated on cooling was collected and crystallised from EtOH.

**N-(2-Bromo-4,5-dimethoxybenzylidene)aniline ( 1a ).** From 6-bromoveratraldehyde[18] and aniline; compound **1a** had mp: 239-241°C; IR 1620 ( C=N ); $^1H$ NMR δ ( 60 MHz ) 3.95, 4.00 ( s, 6H, 2xO*Me* ), 7.10-7.50 ( m, 6H, Ar-*H* ), 7.80 ( s, 1H, Ar-*H* ), 8.80 ( s, 1H, C*H*=N ). Anal. Calcd. for $C_{15}H_{14}BrNO_2$: C, 56.27; H, 4.41; N, 4.37. Found: C, 56.15; H, 4.39; N, 4.26%.

**N-(2-Bromo-4,5-methylenedioxybenzylidene)aniline ( 1b ).** From 6-bromopiperonal[19] and aniline; compound **1b** had mp: 130-131°C; IR ( KBr ) 1610 ( C=N ); $^1H$ NMR ( 60 MHz ) δ 6.10 ( s, 2H, O$CH_2$O ), 7.10 ( s, 1H, Ar-*H* ), 7.20-7.70 ( m, 5H, Ar-*H* ), 7.80 ( 1H, Ar-*H* ), 8.80 ( s, 1H, C*H*=N ). Anal. Calcd. for $C_{14}H_{10}BrNO_2$: C, 55.29; H, 3.31; N, 4.60. Found: C, 55.20; H, 3.29; N, 4.54%.

**N-(2'-Bromo-4',5'-methylenedioxybenzylidene)-2-methoxyaniline ( 1c ).** From 6-bromopiperonal and 2-methoxyaniline; compound **1c** had mp: 138-139°C; IR ( KBr ) 1615 ( C=N ); $^1H$ NMR ( 60 MHz ) δ 3.90 ( s, 3H, O*Me* ), 6.10 ( s, 2H, O$CH_2$O ), 7.00-7.20 ( *m*, 5H, Ar-*H* ), 7.85 ( s, 1H, Ar-*H* ), 8.85 ( s, 1H, C*H*=N ). HREIMS Calcd. for $C_{15}H_{12}BrNO_3$: 333.0000. Found: 332.9993.

**N-(2'-Bromo-4',5'-methylenedioxybenzylidene)-3-methoxyaniline ( 1d ).** From 6-bromopiperonal and 3-methoxyaniline, had mp: 132-134°C; IR ( KBr ) 1615 ( C=N ); $^1H$ NMR ( 60 MHz ) δ 3.90 ( s, 3H, O*Me* ), 6.10 (s, 2H, O$CH_2$O ), 6.75-7.55 ( m, 5H, Ar-*H* ), 7.80 ( s, 1H, Ar-*H* ), 8.85 ( s, 1H, C*H*=N ). Anal. Calcd. for $C_{15}H_{12}BrNO_3$: C, 53.91; H, 3.62; N, 4.19. Found: C, 53.93; H, 3.61; N, 4.15%.

**N-(2'-Bromo-4',5'-methylenedioxybenzylidene)-4-methoxyaniline (1e).** From *o*-bromopiperonal and *p*-anisidine; had mp: 114-115°C; IR ( KBr ) 1615 ( C=N ); $^1$H NMR ( 60 MHz ) δ 3.85 ( s, 3H, O*Me* ), 6.05 ( s, 2H, OC*H*$_2$O ), 6.94 ( d, 2H, *J*=9 Hz, Ar-*H* ), 7.72 ( s, 1H, Ar-*H* ), 8.76 ( s, 1H, C*H*=N ). Anal. Calcd. for $C_{15}H_{12}BrNO_3$: C, 53.91; H, 3.62; N, 4.19. Found: C, 53.88; H, 3.60; N, 4.02%.

**N-(2'-Bromo-4',5'-methylenedioxybenzylidene)-2,4-dimethoxyaniline ( 1f ).** From *o*-bromopiperonal and 2,4-dimethoxyaniline,[20] had mp: 125-127°C; IR ( KBr ) 1620 ( C=N ); $^1$H NMR ( 60 MHz ) δ 3.85 ( s, 3H, O*Me* ), 3.90 (s, 3H, O*Me* ), 6.05 (s, 2H, OC*H*$_2$O), 6.40-6.70 ( m, 2H, Ar-*H* ), 6.95-7.25 (m, 2H, Ar-*H*), 7.80 ( s, 1H, Ar-*H* ), 8.85 ( s, 1H, C*H*=N ). Anal. Calcd. for $C_{16}H_{14}BrNO_4$: C, 52.76; H, 3.87; N, 3.85. Found: C, 52.71; H, 3.86; N, 3.78%.

**N-(2'-Bromo-4',5'-methylenedioxybenzylidene)-3,5-dimethoxyaniline ( 1g ).** From *o*-bromopiperonal and 3,5-dimethoxyaniline,[20] had mp: 130-132°C; IR ( KBr ) 1600 ( C=N ); $^1$H NMR ( 60 MHz ) δ 3.83 ( s, 6H, 2xO*Me* ), 6.05 ( s, 2H, OC*H*$_2$O ), 6.37 ( s, 3H, Ar-*H* ), 7.05 (s, 1H, Ar-*H* ), 7.70 ( s, 1H, Ar-*H* ), 8.72 ( s, 1H, C*H*=N ). HREIMS Calcd. for $C_{16}H_{14}BrNO_4$: 363.0106. Found: 363.0078.

**N-(2'-Bromo-4',5'-methylenedioxybenzylidene)-2,4,5-trimethoxyaniline ( 1h ).** From 6-bromopiperonal and 2,4,5-trimethoxyaniline, had mp: 118-120°C; IR ( $CHCl_3$ ) 1600 ( C=N ); $^1$H NMR ( 60 MHz ) δ 3.90~3.95 ( 9H, 3xO*Me* ), 6.15 ( s, 2H, OC*H*$_2$O), 6.65 ( s, 1H, Ar-*H* ), 6.80 ( s, 1H, Ar-*H*), 7.10 ( s, 1H, Ar-*H* ), 7.80 ( s, 1H, Ar-*H* ), 8.90 ( s, 1H, C*H*=N ). HREIMS Calcd. for $C_{17}H_{16}NO_5Br$ - $CH_3$: 379.9957. Found: 379.9941.

**N-(2'-Bromo-4',5'-methylenedioxybenzylidene)-1-napthylamine ( 1i ).** From 6-bromopiperonal and α-napthylamine,[20] had mp: 116-123°C; IR ( KBr ) 1610 ( C=N ); $^1$H NMR ( 60 MHz ) δ 6.10 ( s, 2H, OC*H*$_2$O ), 7.0-8.1 (m, 9H, Ar-*H* ), 8.9 ( s, 1H, C*H*=N ). Anal. Calcd. for $C_{18}H_{12}BrNO_2$: C, 61.00; H, 3.40; N, 3.95. Found: C, 60.98; H, 3.40; N, 3.79%.

**General Method for the preparation of N-bromobenzyl derivatives ( 2 ).** The amine ( 1 equiv. ) in dry MeOH, was treated with $NaBH_4$ ( 4-8 fold excess ) in portions at RT and after initial vigorous reaction had subsided, the mixture was heated under reflux ( 15 min. ). Upon completion of reduction ( tlc control and disappearance of the yellow colour ), water was added and the secondary amine isolated either by filtration or extraction with ether. They were crystallised from EtOH.

**N-(2-Bromo-4,5-dimethoxybenzyl)aniline ( 2a ).** Had mp: 89-90°C; IR ( KBr ) 3380 ( NH ); $^1$H NMR ( 60 MHz ) δ 3.70 ( s, 3H, O*Me* ), 3.80 ( s, 3H, O*Me* ), 4.25 ( b, s, 3H, C*H*$_2$N*H*, 1H exchangeable in $D_2O$ ), 6.50-7.20 ( m, 7H, Ar-*H* ). Anal. Calcd. for $C_{15}H_{16}BrNO_2$: C, 55.92; H, 5.01; N, 4.35. Found: C, 55.94; H, 5.02; N, 4.48%.

**N-(2-Bromo-4,5-methylenedioxybenzyl)aniline ( 2b ).** Had mp: 90-92°C; IR ( KBr ) 3420 ( NH ); $^1$H NMR ( 60 MHz ) δ 4.20 ( bs, 3H, C*H*$_2$N*H*, 1H exchangeable with $D_2O$ ), 5.85 ( s, 2H, OC*H*$_2$O ),

6.45-7.20 ( m, 7H, Ar-*H* ). Anal. Calcd. for $C_{14}H_{12}BrNO_2$: C, 54.92; H, 3.95; N, 4.57. Found: C, 54.60; H, 3.89; N, 4.55%.

**N-(2'-Bromo-4',5'-methylenedioxybenzyl)-2-methoxyaniline ( 2c ).** Had mp: 87-88°C; IR ( KBr ) 3430 ( NH ); $^1$H NMR ( 60 MHz ) δ 3.9 ( s, 3H, O*Me* ), 4.35 ( bs, 2H, C*H*$_2$NH ), 5.95 ( s, 2H, OC*H*$_2$O ), 6.45-7.15 ( m, 7H, Ar-*H* and N*H*, 1H exchangeable in $D_2O$ ). Anal. Calcd. for $C_{15}H_{14}BrNO_3$: C, 53.59; H, 4.20; N, 4.17. Found: C, 53.64; H, 4.17; N, 4.29%.

**N-(2'-Bromo-4',5'-methylenedioxybenzyl)-3-methoxyaniline ( 2d ).** Had mp: 85-86°C; IR ( KBr ) 3380, 3400 ( NH ); $^1$H NMR ( 300 MHz ) δ 3.75 ( s, 3H, O*Me* ), 4.30 ( bs, 3H, C*H*$_2$N*H*, 1H exchangeable in $D_2O$ ), 6.00 ( s, 2H, OC*H*$_2$O ), 6.15-6.50 ( m, 3H, Ar-*H* ), 6.90-7.20 ( m, 3H, Ar-*H* ). Anal. Calcd. for $C_{15}H_{14}BrNO_3$: C, 53.59; H, 4.20; N, 4.17. Found: C, 53.66; H, 4.21; N, 4.20%.

**N-(2'-Bromo-4',5'-methylenedioxybenzyl)-4-methoxyaniline ( 2e ).** Had mp: 103.5-106°C; IR ( KBr ) 3380 ( NH ); $^1$H NMR ( 300 MHz ) δ 3.73 ( s, 3H, O*Me* ), 3.92 ( bs, 1H, N*H*, exchangeable in $D_2O$ ), 4.25 ( s, 2H, C*H*$_2$NH ), 5.94 ( s, 2H, OC*H*$_2$O ), 6.56 ( d, 2H, *J* =8.7 Hz, Ar-*H* ), 6.77 (d, 2H, *J* =8.7 Hz, Ar-*H* ), 6.91 ( s, 1H, Ar-*H* ), 7.01 ( s, 1H, Ar-*H* ). Anal. Calcd. for $C_{15}H_{14}BrNO_3$: C, 53.59; H, 4.20; N, 4.17. Found: C, 53.60; H, 4.18; N, 4.08%.

**N-(2'-Bromo-4',5'-methylenedioxybenzyl)-2,4-dimethoxyaniline ( 2f ).** Had mp: 129-130°C; IR ( KBr ) 3560, 3480, 3430 ( NH ); $^1$H NMR ( 300 MHz ) δ 3.70 ( s, 3H, O*Me* ), 3.80 ( s, 3H, O*Me* ), 4.25 ( bs, 3H, C*H*$_2$N*H*, 1H exchangeable in $D_2O$ ), 5.90 ( s, 2H, OC*H*$_2$O ), 6.40 ( m, 3H, Ar-*H* ), 6.90 ( s, 1H, Ar-*H* ), 7.00 ( s, 1H, Ar-*H* ). Anal. Calcd. for $C_{16}H_{16}BrNO_4$: C, 52.48; H, 4.40; N, 3.82. Found: C, 52.31; H, 4.30; N, 3.66%.

**N-(2'-Bromo-4',5'-methylenedioxybenzyl)-3,5-dimethoxyaniline ( 2g ).** Had mp: 107-109°C; IR ( KBr ) 3330 ( NH ); $^1$H NMR ( 300 MHz ) δ 3.73 ( s, 3H, O*Me* ), 4.185 ( bs, 1H, N*H*, exchangeable in $D_2O$ ), 4.27 ( s, 2H, C*H*$_2$NH ), 5.78 ( d, 2H, *J*=2.1 Hz, Ar-*H* ), 5.89 ( t, 1H, *J*=2.1 Hz, Ar-*H* ), 5.94 ( s, 2H, OC*H*$_2$O ), 6.89 ( s, 1H, Ar-*H* ), 7.00 ( s, 1H, Ar-*H* ). HREIMS Calcd. for $C_{16}H_{16}BrNO_4$: 365.0263. Found: 365.0285.

**N-(2'-Bromo-4',5'-methylenedioxybenzyl)-2,4,5-trimethoxyaniline ( 2h ).** Had mp: 66-71°C; IR ( $CHCl_3$ ) 3680, 3620, 3420 ( NH ); $^1$H NMR ( 300 MHz ) δ 3.75 ( s, 3H, O*Me* ), 3.85 ( s, 6H, 2xO*Me* ), 4.35 (bs, 3H, C*H*$_2$N*H*, 1H exchangeable in $D_2O$ ), 5.95 ( s, 2H, C*H*$_2$O ), 6.25 ( s, 1H, Ar-*H* ), 6.60 ( s, 1H, Ar-*H* ), 6.95 ( s, 1H, Ar-*H* ), 7.05 ( s, 1H, Ar-*H* ). Anal. Calcd. for $C_{17}H_{18}BrNO_5$: C, 51.59; H, 4.69; N, 3.53. Found: C, 51.89; H, 4.67; N, 3.37%.

**N-(2'-Bromo-4',5'-methylenedioxybenzyl)-1-naphthylamine ( 2i ).** Had mp: 100-102°C; IR ( KBr ) 3440 ( NH ); $^1$H NMR ( 60 MHz ) δ 4.50 ( bs, 2H, C*H*$_2$NH ), 4.80 ( bs, 1H, N*H*, exchangeable in $D_2O$ ), 5.95 ( s, 2H, C*H*$_2$O ), 6.45-8.10 (m, 9H, Ar-*H* ). Anal. Calcd. for $C_{18}H_{14}BrNO_2$: C, 60.70; H, 3.96; N, 3.90. Found: C, 60.66; H, 3.93; N, 3.74%.

**N-(2'-Bromobenzyl)-3,4-methylenedioxyaniline ( 2j ).** 3,4-Methylenedioxyaniline[20] ( 5.5 g; 0.04 mol ) in dry THF ( 20 ml ) was mixed with NaH ( 0.8 g, 0.02 mol ) and the mixture after being stirred at RT ( 1 hr ) was treated with *o*-bromobenzyl bromide ( 5 g; 0.02 mol ) in dry THF ( 15 ml ). On completion of the reaction ( 3 days, RT ), water was added and the product taken up in ether. Extraction with dil HCl ( 5% ) followed by basification to pH=12 liberated the amine which was reextracted with ether, washed with water and dried ( $Na_2SO_4$ ). Evaporation of the solvent and purification of the residue by chromatography yield the amine ( 4.5 g; 74% yield ) mp: 65-66°C ( from EtOH ); $^1$H NMR ( 60 MHz ) δ 3.85 ( bs, 1H, N*H* exchangeable in $D_2O$ ), 4.30 ( s, 2H, C*H*$_2$NH ), 5.85 ( s, 2H, OC*H*$_2$O ), 6.05 ( dd, 1H, *J*=8.7 and 2.7 Hz, Ar-*H* ), 6.25 ( d, 1H, *J*=2.7 Hz, Ar-*H* ), 6.65 ( d, 1H, *J*=8.7 Hz, Ar-*H* ), 6.90-7.75 ( m, 4H, Ar-*H* ). Anal. Calcd. for $C_{14}H_{12}BrNO_2$: C, 54.92; H, 3.95; N, 4.57. Found: C, 54.95; H, 3.89; N, 4.46%.

**N-(2'-Bromobenzyl-4',5'-methylenedioxybenzyl)-2,5-dimethoxyaniline ( 2k ).** 2,5-Dimethoxyaniline HCl[20] ( 1.62 g ) and $NaHCO_3$ ( 2.02 g ) in isopropanol were treated with 2-bromo-3,4-methylenedioxybenzyl chloride ( 1.42 g ) in isopropanol and the mixture allowed to stand at RT ( 13 days ). Evaporation of the solvent yielded a residue which was purified by chromatography. The title compound **2l** obtained as white crystals ( 37% yield ) had mp: 98-101°C ( from EtOH ); IR 3450, 3420 ( NH ); $^1$H NMR ( $CD_3CN$; 300 MHz ) δ 3.63 ( s, 3H, O*Me* ), 3.78 ( s, 3H, O*Me* ), 4.28 ( s, 2H, C*H*$_2$NH ), 5.03 ( bs, 1H, N*H*, exchangeable in $D_2O$ ), 6.02 ( s+dd, 4H, *J*=8.4 Hz, OC*H*$_2$O+Ar*H* ), 6.69 ( d, 1H, *J*=8.4 Hz, Ar-*H* ), 6.83 ( s, 1H, Ar-*H* ), 7.05 ( s, 1H, Ar-*H* ). Anal. Calcd. for $C_{16}H_{16}BrNO_4$: C, 52.48; H, 4.40; N, 3.82. Found: C, 52.54; H, 4.35; N, 3.75%.

**N-(2'-Bromobenzyl)-N,N-diphenylamine ( 2l ).** Prepared as described for **2j**, except that the mixture was refluxed ( 20 h ). The crude product obtained on evaporation of THF, was chromatographed ( $SiO_2$ ; *n*-hexane ) givining the tertiary amine ( 21% yield ), mp: 78-80°C ( from MeOH ); $^1$H NMR ( 60 MHz ) δ 5.10 ( s, 2*H*, C*H*$_2$N ), 6.80-7.90 ( m, 14H, Ar-*H* ). Anal. Calcd. for $C_{19}H_{16}BrN$: C, 67.47; H, 4.77; N, 4.07. Found: C, 67.66; H, 4.75; N, 4.07%.

**N-(2'-Bromobenzyl)-2,3-dihydroindole ( 2m ).** 2,3-Dihydroindole[20] ( 8.34 g ; 0.07 mol ) in ether ( 30 ml ), cooled in an ice bath, was treated with stirring with a solution of 2-bromobenzyl bromide ( 9.96 g, 0.04 mol ) in ether ( 30 ml ). The mixture was stirred ( RT ; 1 h ) and then filtered. The solid obtained on evaporation of the solvent from the filtrate, was purified by chromatography ( $SiO_2$ ; $CH_2Cl_2$ ) to give the tertiary amine **2n** ( 10.77 g ; 97% yield ), mp: 40°C; $^1$H NMR ( 60 MHz ) δ 2.75-3.60 ( m, 4*H*, C*H*$_2$C*H*$_2$N ), 4.25 ( s, 2H, ArC*H*$_2$N ), 6.20-7.60 ( m, 8H, Ar-*H* ). Anal. Calcd. for $C_{15}H_{14}BrN$: C, 62.52; H, 4.90; N, 4.86. Found: C, 62.58; H, 4.93; N, 4.96%.

**N-(2-Bromobenzyl)indole ( 2n ).** Was obtained in 70% yield from indole by N-alkylation with *o*-bromobenzyl bromide under phase transfer conditions[21] using Adogen 464, had mp: 50-53°C ( from EtOH ); $^1$H NMR ( 60 MHz ) δ 5.45 ( s, 2*H*, C*H*$_2$N ), 6.50-7.90 ( m, 10H, Ar-*H* ). Anal. Calcd. for $C_{16}H_{12}BrNO_2$: C, 62.96; H, 4.23; N, 4.89. Found: C, 62.75; H, 4.13; N, 4.82%.

**General Method for the preparation of phenanthridines.** The appropriate bromide ( 1 equiv. ), and TBTH ( 1 to 2 mol equiv. ) in dry benzene ( 240 ml ), under reflux, was treated with AIBN ( 0.5 to 0.6 mol equiv. ) in benzene ( 58 ml ), in portions during *ca* 16 h. Evaporation of the solvent under reduced pressure left an oily residue which was processed in one of the following three methods to isolate the products:

**i.** The residue remaining after repeated washings with *n*-pentane, to remove organotin species, was submitted to column chromatography ( $SiO_2$ ) using $CH_2Cl_2$-MeOH ( 2% ; v/v ) as eluent.

**ii.** The residue dissolved in $Et_2O$ was treated with an aqueous solution of KF, the solid formed removed by filtration[22] and the products contained in the filtrate isolated by chromatography.

**iii.** The residue was dissolved in acetonitrile[23] and the solution washed several times with *n*-hexane, the combined *n*-hexane fractions extracted once with $CH_3CN$. Evaporation of the acetonitrile solutions yielded a residue which was subjected to column chromatography.

**8,9-Dimethoxyphenanthridine ( 3a ).** From **2a**, using method **i** or **ii** had mp: 165-166°C ( from benzene ), ( lit. mp:[3b] 163-164°C ); IR ( KBr ) 1590 ( C=N ); $^1$H NMR ( 60 MHz ) δ 4.10 ( s, 3H, O*Me* ), 4.15 ( s, 3H, O*Me* ), 7.35-8.60 ( m, 6H, Ar-*H* ), 9.20 ( s, 1H, C*H*=N ).

**8,9-Methylenedioxyphenanthridine ( 3b ).** From **2b**, using method **i** or **ii** had mp: 140-141°C ( from *n*-hexane; mp:[24,3b] 138-139°C; m.m.p. 140-141°C ); IR ( KBr ) 1580 ( C=N ); $^1$H NMR ( 60 MHz ) δ 6.25 ( s, 2H, O$CH_2$O ), 7.4-8.70 ( m, 6H, Ar-*H* ), 9.25 ( s, 1H, C*H*=N ).

**4-Methoxy-8,9-methylenedioxyphenanthridine ( 3c ).** From **2c**, using method **i** had mp: 229-231°C ( after sublimation ); IR ( KBr ) 1605 ( C=N ); $^1$H NMR ( 400 MHz ) δ 4.12 ( s, 3H, O*Me* ), 6.16 ( s, 2H, O$CH_2$O ), 7.09 ( d, 1H, *J*=8.1 Hz, Ar-*H* ), 7.34 (s, 1H, Ar-*H* ), 7.55 ( t, 1H, *J*=8.1 Hz, Ar-*H* ), 7.87 ( s, 1H, Ar-*H* ), 7.94 ( d, 1H, *J*=8.1 Hz, Ar-*H*), 9.11 ( s, 1H, C*H*=N ). HREIMS Calcd. for $C_{15}H_{11}NO_3$: 253.0709. Found: 253.0744.

**1-Methoxy-8,9-methylenedioxyphenanthridine ( 3d ).** From **2d** using method **i**, had mp: 193-195°C ( from benzene ); IR ( KBr ) 1584 (C=N ); $^1$H NMR ( 300 MHz ) δ 4.12 ( s, 3*H*, O*Me* ), 6.16 ( s, 2H, O$CH_2$O ), 7.09 ( d, 1H, *J*=8.1 Hz, Ar-*H* ), 7.33 ( s, 1H, Ar-*H* ), 7.60 ( t, 1H, *J*=8.1 Hz, Ar-*H* ), 7.79 ( d, 1H, *J*=8.1 Hz, Ar-*H* ), 8.95 ( s, 1H, Ar-*H* ), 9.05 ( s, 1H, C*H*=N ). HREIMS Calcd. for $C_{15}H_{11}NO_3$: 253.0744. Found: 253.0744.

**3-Methoxy-8,9-methylenedioxyphenanthridine ( 3d' ).** From **2d** using method **i**, had mp: 185-188°C ( from benzene ); IR ( KBr ) 1596 (C=N ); $^1$H NMR ( 300 MHz ) δ 3.97 ( s, 3*H*, O*Me* ), 6.14 ( s, 2H, O$CH_2$O ), 7.26 (s+dd, 3H, *J*=9.3 and 2.7 Hz, Ar-*H* ), 7.52 ( d, 1H, *J*=2.7 Hz, Ar-*H* ), 7.78 ( s, 1H, Ar-*H* ), 8.23 ( d, 1H, *J*=9.3 Hz, Ar-*H* ), 9.03 (s, 1H, C*H*=N ). HREIMS Calcd. for $C_{15}H_{11}NO_3$: 253.0739. Found: 253.0749.

**2-Methoxy-8,9-methylenedioxyphenanthridine ( 3e ).** From **2e**, using method **i**, had mp: 210-214°C ( after sublimation; mp:[3a,25] 211-215°C ); IR ( KBr ) 1580 (C=N ); $^1$H NMR ( 300 MHz ) δ 4.01 ( s, 3H, O*Me* ), 6.17 ( s, 2H, O$CH_2$O ), 7.32 ( s+dd, 2H, *J*=8.7 and 2.7 Hz, Ar-*H* ), 7.65 ( d, 1H, *J*=2.7 Hz, Ar-*H* ),

7.80 ( s, 1H, Ar-*H* ), 8.05 ( d, 1H, *J*=8.7 Hz, Ar-*H* ), 7.80 ( s, 1H, Ar-*H* ), 8.05 ( d, 1H, *J*=8.7 Hz, Ar-*H* ), 8.95 ( s, 1H, C*H*=N ).

**2,4-Dimethoxy-8,9-methylenedioxyphenanthridine ( 3f ).** From **2f**, using method **i**, had mp: 220-224°C ( from benzene ); IR ( KBr ) 1590 (C=N ); $^1$H NMR ( 300 MHz ) δ 3.99 ( s, 3H, O*Me* ), 4.08 ( s, 3H, O*Me* ), 6.15 ( s, 2H, OC$H_2$O ), 6.73 ( d, 1H, *J*=2.1 Hz, Ar-*H* ), 7.20 ( d, 1H, *J*=2.1 Hz, Ar-*H* ), 7.29 ( s, 1H, Ar-*H* ), 7.76 ( s, 1H, Ar-*H* ), 8.97 ( s, 1H, C*H*=N ). Anal. Calcd. for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.92. Found: C, 68.00; H, 4.62; N, 4.62%.

**1,3-Dimethoxy-8,9-methylenedioxyphenanthridine ( 3g ).** From **2g**, using method **i**, had mp: 255-256°C ( from benzene ); IR ( KBr ) 1596 (C=N ); $^1$H NMR ( 300 MHz ) δ 3.96 ( s, 3H, O*Me* ), 4.08 ( s, 3H, O*Me* ), 6.14 ( s, 2H, OC$H_2$O ), 6.72 ( d, 1H, *J*=2.4 Hz, Ar-*H* ), 7.20 ( d, 1H, *J*=2.4 Hz, Ar-*H* ), 7.29 ( s, 1H, Ar-*H* ), 8.81 ( s, 1H, Ar-*H* ), 8.99 ( s, 1H, C*H*=N ). Anal. Calcd. for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.94. Found: C, 67.64; H, 4.56; N, 4.83%.

**1,2,4-Trimethoxy-8,9-methylenedioxyphenanthridine ( 3h ).** From **2h**, using method **i**, had mp: 188-190°C ( from benzene ); IR ( KBr ) 1600 (C=N ); $^1$H NMR ( 300 MHz ) δ 3.90 ( s, 3H, O*Me* ), 4.06 ( s, 3H, O*Me* ), 4.12 ( s, 3H, O*Me* ), 6.16 ( s, 2H, OC$H_2$O ), 6.90 ( s, 1H, Ar-*H* ), 7.32 ( s, 1H, Ar-*H* ), 8.94 ( s, 1H, Ar-*H* ), 8.95 ( s, 1H, C*H*=N ). HREIMS Calcd. for $C_{17}H_{15}NO_5$: 313.0950. Found: 313.0955.

**8,9-Methylenedioxybenzo(*c*)phenanthridine ( 3i ).** From **2i**, using method **i**, had mp: 235-236°C ( from benzene; mp:[3a] 236-238°C ).

**2,3-Methylenedioxyphenanthridine ( 3j ).** From **2j**, using method **iii**, had mp: 190-192°C ( from MeOH ); IR ( KBr ) 1588 (C=N ); $^1$H NMR ( 300 MHz ) δ 6.15 ( s, 2H, OC$H_2$O ), 7.53 ( s, 1H, Ar-*H* ), 7.63 (dt, 1H, *J*=7.5 and 0.9 Hz, Ar-*H* ), 7.80 ( dt, 1H, *J*=8.4 and 1.5 Hz, Ar-*H* ), 7.66 ( s, 1H, Ar-*H* ), 8.00 ( d, 1H, *J*=7.5 Hz, Ar-*H* ), 8.38 ( d, 1H, *J*=8.4 Hz, Ar-*H* ), 9.15 ( s, 1H, C*H*=N ). Anal. Calcd. for $C_{14}H_9NO_2$: C, 75.33; H, 4.06; N, 6.27. Found: C, 75.31; H, 3.95; N, 6.11%.

**1,4-Dimethoxy-8,9-methylenedioxyphenanthridine ( 3k ).** From **2k**, using method **i**, had mp: 177-178°C ( from benzene ); IR ( KBr ) 1630 (C=N ); $^1$H NMR ( 300 MHz ) δ 4.07 ( s, 3H, O*Me* ), 4.08 ( s, 3H, O*Me* ), 6.16 ( s, 2H, OC$H_2$O ), 7.03 ( s, 1H, Ar-*H* ), 7.04 ( s, 1H, Ar-*H* ), 7.36 ( s, 1H, Ar-*H* ), 9.013 ( s, 1H, Ar-*H* ), 9.121 ( s, 1H, C*H*=N ). HREIMS Calcd. for $C_{16}H_{13}NO_4$: 283.0844. Found: 283.0840.

**10b,11-Dihydro-6H-isoindolo(2,1-*a*)indole ( 5**, R = H ). From **2n**, using method **iii**, had mp: 82-85°C ( from EtOH ); $^1$H NMR ( 300 MHz ) δ 3.36 ( dd, 1H, *J*=16.2 and 3 Hz, C$H_A$H$_B$CH ), 3.53 ( dd, 1H, *J*=16.2 and 9.9 Hz, CH$_A$H$_B$CH ), 4.50 ( d, 1H, *J*=15 Hz, C$H_2$N ), 4.63 ( dd, 1H, *J*=15 and 1.8 Hz, C$H_2$N ), 5.20 ( d, 1H, *J*=9.9 Hz, CH$_2$C*H* ), 6.76 ( d, 1H, *J*=7.5 Hz, Ar-*H* ), 6.80 ( d, 1H, *J*=6.9 Hz, Ar-*H* ), 7.06 ( d, 1H, *J*=6.9 Hz, Ar-*H* ), 7.11 ( d, 1H, *J*=7.5 Hz, Ar-*H* ), 7.18-7.30 ( m, 4H, Ar-*H* ). Anal. Calcd. for $C_{13}H_{13}N$: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.70; H, 6.25; N, 6.65%.

**6H-isoindolo(2,1-*a*)indole** ( **6**, R = H ). Had mp: 228-231°C ( from EtOH ); $^1$H NMR ( 300 MHz ) δ 5.06 ( s, 2H, C*H*$_2$N ), 6.62 ( s, 1H, Ar-*H* ), 7.10 ( t, 1H, *J*=7.5 Hz, Ar-*H* ), 7.2 ( t, 1H, *J*=7.5 Hz, Ar-*H* ), 7.25 ( s, 1H, Ar-*H* ), 7.31 ( d, 1H, *J*=7.8 Hz, Ar-*H* ), 7.37 ( t, 1H, *J*=7.8 Hz, Ar-*H* ), 7.47 ( d, 1H, *J*=7.5 Hz, Ar-*H* ), 7.66 ( d, 1H, *J*=7.8 Hz, Ar-*H* ), 7.70 ( d, 1H, *J*=7.5 Hz, Ar-*H* ). Anal. Calcd. for $C_{15}H_{11}N$: C, 87.77; H, 5.40; N, 6.82. Found: C, 87.82; H, 5.41; N, 6.74%.

**N-Benzyl-2,3-dihydroindole ( 7 ) and N-benzylindole.** From **2m**, using method **i** were obtained the dihydroindole **7** as a yellow oil; $^1$H NMR ( 60 MHz ) δ 2.75-3.55 ( m, 4H, C*H*$_2$CH$_2$N + CH$_2$C*H*$_2$N ), 4.30 ( s, 2H, C*H*$_2$Ar ), 6.45-7.80 ( m, 9H, Ar-*H* ) and *N-benzylindole*, $^1$H NMR ( 300 MHz, CD$_3$CN ) δ 5.36 ( s, 2H, C*H*$_2$N ), 6.50 ( d, 1H, *J*=3 Hz ), 7.00-7.34 ( m, 9H, Ar-*H* ), 7.58 ( d, 1H, *J*=3 Hz ).

**N-Phenyl-6-oxo-5,6-dihydrophenanthridine.** From **2l**, using method **iii**, had mp: 224-225°C ( from EtOH, lit[15] mp: 226°C ) and possessing infrared and $^1$NMR spectra identical with those of an authentic sample.

## REFERENCES AND NOTES


1. a) Giese, B. *Radical in Organic Synthesis; Formation of C-C Bonds*, Pergamon Press; New York, 1986;
   b) For a recent review containing copious examples of application of radical chemistry to natural product synthesis, see: Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chem. Rev.*, **1991**, *91*, 1237.
2. a) Narasimhan, N. S.; Aiden, I. S. *Tetrahedron Lett.*, **1988**, *29*, 2987;
   b) Togo, H.; Kikuchi, O., *Tetrahedron Lett.*, **1988**, *29*, 4133;
   c) Rosa, A. M.; Prabhakar, S.; Lobo, A. M. *Tetrahedron Lett.*, **1990**, *31*, 1881;
   d) Motherwell, W. B.; Pennell, A. M. K. *J. Chem. Soc., Chem. Commun*, **1991**, 877.
3. a) For other general synthetic methods involving $C_{aryl}$-$C_{aryl}$ bond formation see: a) Siddiqui, M. A.; Snieckus, V. A. *Tetrahedron Lett.*, **1988**, *28*, 5463;
   b) Kessar, S. V.; Pal, D.; Singh, M. *Tetrahedron*, **1973**, *29*, 177;
   c) For the occurrence of dialkoxyphenanthridines such as 6,7-methylenedioxyphenanthridine and its methochloride in nature, see: Suau, R.; Gómez, A. I.; Rico, R. *Phytochemistry*, **1990**, *29*, 1710.
4. This work was partially presented at the VII$^{th}$ FECHEM Conference on Heterocycles in Bio-Organic Chemistry, held in Santiago de Compostela ( Spain ), on 26-29/9/1993.
5. a) Cushman, M.; Mohan, P.; Smith, E. C. R. *J. Med. Chem.*, **1984**, *27*, 544;
   b) Messmer, W. M.; Tin-Wa, M.; Fong, H. H. S.; Bevelle, C.; Farnsworth, N. R.; Abraham, D. J.; Trojanek, J. *J. Pharm. Sci.*, **1972**, *61*, 1858.
6. For a lengthy synthesis of **5** (R=OH ; R=OMe), see: Takada, T.; Ohki, S. *Chem. Pharm. Bull. (Jpn)*, **1971**, *19*, 977.
7. A similar radical, photochemically generated from N-(*o*-halobenzyl)aniline, has been reported to give, among other products, a low yield ( 15% ) of the 5,6-dihydrophenanthridine: Mizuno, K.; Pac, C.; Sukurai, H. *Bull. Chem. Soc. Jpn.*, **1973**, *46*, 3316.
8. Firestone, R. A. *J. Org. Chem.*, **1969**, *34*, 2621.
9. For geometric reasons alkenylaryl radicals incorporating a hetero atom (O or N) in the side chain are expected to afford mainly product of 1,5 cyclisations and this was experimentally observed to be so in the

case of oxygen. It is also known that in systems with all carbon framework the kinetically preferred *5-exo* cyclisation is retarded by the presence of a substituent at the C atom suffering the radical attack (Beckwith, A. L. J. *Tetrahedron*, **1981**, *37*, 3073) and as a consequence the competing *6-endo* addition becomes significant or occasionally even exclusive (Padwa, A.; Murphee, S. S.; Yeske, P. E. *Tetrahedron Lett.*, **1990**, *31*, 2983; Urabe, H. Kuwajima, I. *Tetrahedron Lett.*, **1986**, *27*, 1355).

10. Leardini, R.; Nanni, D.; Pedulli, G. F.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Perkin Trans 1*, **1986**, 1591.
11. The presence of 5,6-dihydrophenanthridines could indeed be detected in all these reactions on the tlc plates. However, they are rapidly oxidised under aerobic conditions.
12. a) Bhacca, N. S.; Johnson, L. F.; Shoolery, J. N. NMR Catalog; Spec. no. 349, Varian Associates, Palo Alto, 1962;
    b) Blanco, O.; Castedo, L.; Cid, M.; Seijas, J. A.; Vilaverde, C. *Heterocycles*, **1990**, *31*, 1077.
13. For a reference to intrusion of reversibility in an intramolecular aryl-aryl radical coupling reaction, not involving an EWG group ortho to the $\sigma$ radical, see: Benati, L.; Montevecchi, P. C.; Tundo, A. *J. Chem. Soc., Chem. Commun*, **1978**, 530.
14. a) Bowman, W. R.; Heaney, H.; Jordan, B. J. *Tetrahedron*, **1991**, *48*, 10119.
    b) Curran, D. P.; Yu, H.; Liu, H. *Tetrahedron*, **1994**, *50*, 7343.
    c) Beckwith, A. L. J.; Storey, J. M. D. *J. Chem. Soc., Chem. Commun*, **1995**, 977.
15. Abramovitch, R. A.; Shi, Q. *Heterocycles*, **1994**, *37*, 1463.
16. Curran, D. P.; Liu, H. *J. Chem. Soc., Perkin Trans 1*, **1994**, 1377.
17. Benington, F.; Morin, R. D.; Clark, L. C. *J. Org. Chem.*, **1958**, *23*, 19.
18. Wheeler, T. S.; Naik, R. G. *J. Chem. Soc.*, **1938**, 1780.
19. Becker, D.; Hughes, L. R.; Raphael, R. A. *J. Chem. Soc., Perkin Trans 1*, **1977**, 1674.
20. Supplied by Aldrich Co., Spain.
21. Bocchi, V.; Casnati, G.; Dossena, A.; Villani, F. *Synthesis*, **1976**, 414.
22. Leibner, J. F.; Jacobus, J. *J. Org. Chem.*, **1979**, *44*, 449.
23. Berge, J. M.; Roberts, S. M. *Synthesis*, **1979**, 471.
24. Warren, F. L.; Wright, W. G. *J. Chem. Soc.*, **1958**, 4696; see also ref. 3b.
25. Onaka, T.; Kanda, Y.; Natsume, M. *Tetrahedron Lett.*, **1974**, 1179.

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