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On Attempted Oxidative Cyclisation of Isomeric N,N'-Diphenylphenylenediamines and Their N,N'-Dimethyl Derivatives by Palladium(II) Acetate and Uv Light

Manas Chakrabarty [a] , Archana Batabyal [b] & Shampa Khasnobis [c]

[a] Dept. of Chemistry, Bose Institute, 93/1, A.P.C. Road, Calcutta, 700009, India

[b] Dept. of Chemistry, St. Paul's College, Calcutta, 700009

[c] Dept. of Chemistry, A.J.C. Bose College, Calcutta, 700020, India

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ON ATTEMPTED OXIDATIVE CYCLISATION OF ISOMERIC *N,N'*-DIPHENYLPHENYLENEDIAMINES AND THEIR *N,N'*-DIMETHYL DERIVATIVES BY PALLADIUM(II) ACETATE AND UV LIGHT

Manas Chakrabarty*, Archana Batabyal# and Shampa Khasnobis≠

Dept. of Chemistry, Bose Institute, 93/1, A.P.C. Road, Calcutta 700009, India
Present addresses : #Dept. of Chemistry, St. Paul's College, Calcutta 700009
≠Dept. of Chemistry, A.J.C. Bose College, Calcutta 700020, India

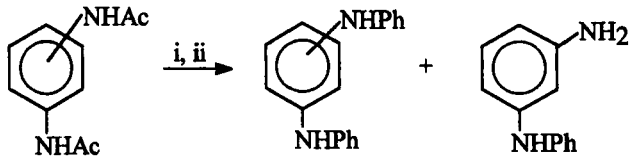
The cyclisation of *N,N'*-diphenyl-*o*-, *m*- and *p*-phenylenediamines and their *N,N'*-dimethyl derivatives by palladium(II) acetate and UV light separately led to both bis-cyclisation, furnishing indolocarbazoles, and mono-cyclisations with cleavage as well as retention of one substituent, producing substituted carbazoles.

Indolocarbazoles (ICs) isolated from soil microbes, blue-green algae and a slime mould display antitumour, antihypertensive, antifungal and antimicrobial properties and inhibit protein kinases[1,2a] and topoisomerases.[2b] The first isolation of ICs, two new and several known, from a marine source has just been published.[3] All these ICs contain a fused indolo[2,3-*a*]carbazole nucleus which is only one of the five possible IC isomers. The latter have already been synthesised but through different routes.[4] With a view to preparing all the IC isomers through a single approach, the biscyclodehydrogenation of *N,N'*-diphenyl-*o*-, *m*- and *p*-phenylenediamines (DPDs;

*To whom correspondence should be addressed

2a-c) and their *N,N'*-dimethyl derivatives (DDPDs; **6a-c**) by palladium(II) acetate in acetic acid and UV light separately was attempted. These reagents are known to bring about the cyclisation of diphenylamines to carbazoles.[5,6] The results of our attempts have been briefly reported in this communication.

The DPDs (**2a-c**) were prepared by the Goldberg coupling[7a-c] of the *N,N'*-diacetyl derivatives (**1a-c**) of the respective phenylenediamines (PDs) with bromobenzene using copper bronze as catalyst, followed by alkaline hydrolysis of the resulting unisolated *N,N'*-diacetyl-DPDs (Scheme 1). Although the yield of *o*-DPD (**2a**) was acceptable (60%), the yield of *p*-DPD (**2c**) was low (30%), while the *meta*-isomer (**1b**) furnished *m*-DPD (**2b**) along with monophenyl-m-PD (3) as a byproduct in 3:1 ratio. The yields of all the DPDs could, however, be significantly improved (vide Experimental) by using cuprous iodide[7d-f] instead of copper bronze.



N, N'-Diacetyl-PDs (**1a-c**) | DPDs (**2a-c**) | **3** (from **1b**)

Throughout : **a**: *o*-; **b**: *m*-; **c**: *p*-

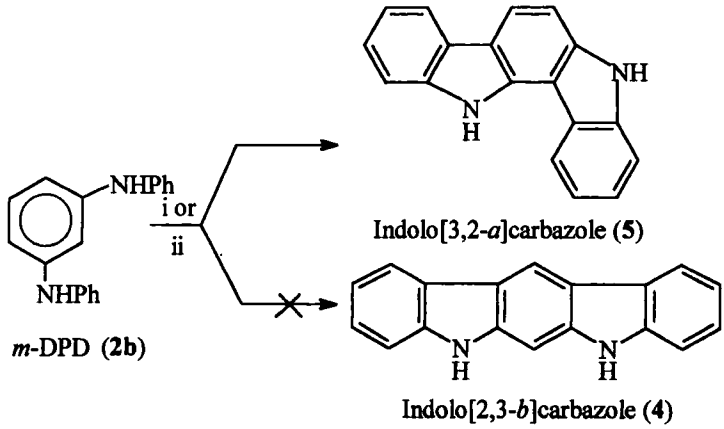
(i) PhBr, Cu-bronze (or Cu_2I_2), K_2CO_3, N_2 , Δ

(ii) KOH-EtOH , Δ ; $H_3O^{\oplus}$

Scheme 1

For the cyclisation of *m*-DPD (**2b**), it was refluxed with palladium(II) acetate (2 equiv) in acetic acid, which furnished an IC, $C_{18}H_{12}N_2$. The product could be

either the linear IC **4** or the angular IC **5**, both of which are known in the literature. It was identified as indolo[3,2-*a*]carbazole (**5**) by comparing its m.p. (299-300°C) with those reported for **4** (348-350°C)[4] and **5** (299-300°C)[8] (Scheme 2). Its ^{1}H and ^{13}C NMR data, not reported earlier, have been presented in this communication (vide Experimental).



(i) : $Pd(OAc)_2$ (2 equiv), HOAc, 1 hr

(ii) : hν (16 Watt), MeOH, I_2 (cat), rt, 40 hr

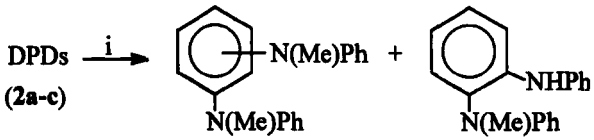
Scheme 2

The same product was obtained in lower yield when a methanolic solution of *m*-DPD (**2b**) was irradiated with low power (16 Watt) UV light at rt using iodine as catalyst (Scheme 2). The use of a larger concn. of iodine or of a higher power (400 Watt) UV source simply led to total decomposition.

The low yield (16%) of **5** was not entirely unexpected, since the palladium-mediated oxidation of diphenylamines has recently been demonstrated to produce

carbazoles as only minor products.[9] Pertinently, it had been previously reported[10] that the vapour phase bis-cyclodehydrogenation of **2b** by 2% Pt-MgO at 500±10°C for 2 hr furnished the linear isomer **4** in 3% yield.

Both *ortho*- and *para*-DPDs (**2a, 2c**) in solution were found to be inert to UV irradiation and completely decomposed when they were treated with palladium(II) acetate in acetic acid. In order to overcome these failures, *N,N'*-dimethyl-DPDs (DDPDs; **6a-c**) were decided to be used as substrates. Both the Eschweiler-Clarke reaction (formaldehyde, formic acid)[11] and sodium borohydride in methanol[12] proved to unsuccessful for this purpose. But the procedure of reductive methylation using formaldehyde, acetic acid and sodium cyanoborohydride in acetonitrile[13] turned out to be a success. The three isomeric DDPDs were obtained in *ca.* 40-97% yields (Scheme 3). Only from *ortho*-DPD (**2a**), the undesired monomethyl derivative **7** was obtained as a major (57%) byproduct.



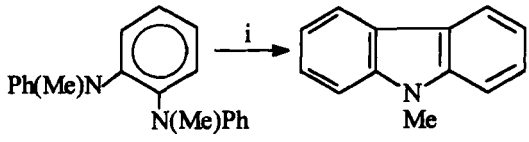
(i): CH_2O, CH_3CN, $NaBH_3CN$, HOAc, rt, 1.5 hr

Scheme 3

To our surprise, the separate treatment of both *ortho*- and *para*-DDPDs (**6a,c**) with the palladium reagent again resulted in decomposition. No attempt was, therefore, made to try this reagent with *meta*-DDPD (**6b**).

The separate exposure of the three DDPDs in solution to UV light using a medium pressure mercury lamp furnished diverse results. Thus, from *ortho*-DDPD (**6a**) in

ether, *N*-methylcarbazole (**8**) was isolated as the sole product in moderate yield (Scheme 4).



6a **8**

(i) : hv (400 W), Et_2O, rt, 11 hr; 41%.

Scheme 4

Monocyclisation with concomitant cleavage of an *ortho*-substituent was thus the only course of the reaction. This is the first report of the loss of an *ortho*-substituent during photocyclisation in the field of DDPDs. Such cleavages have previously been recorded during the photocyclisation of other classes of compounds, viz. stilbenes,[14] styrylnaphthalenes[15] and benzanilides.[16]

From *meta*-DDPD (**6b**) in petrol, two products were obtained, which were identified as 9-methyl-2/4-(*N*-methylanilino)carbazole (26%) and 2/4-anilino-9-methylcarbazole (15%) by analysing their mass and ^1H NMR spectral data.

In order to determine the sites of substitution - C-2 or C-4 - in the two products, the ^{13}C, ^1H-^1H COSY, HETCOR and HMBC spectra of the minor product were analysed. The observed HMBC correlations (Fig. 1) of H-1 and H-3 (δ 7.1, 2H) with C-1, C-3 (δ 109.1, 102.5) and C-4 (δ 114.2) and of H-2 (δ 7.4) with C-4 (δ 138.8) and C-9a (δ 142.5) settled C-4 as the point of substitution. The minor product was thus identified as 4-anilino-9-methylcarbazole (**9**) (Scheme 5). The individual ^1H and ^{13}C NMR assignments of **9** were also ascertained.

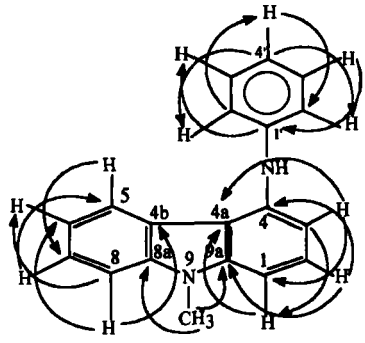
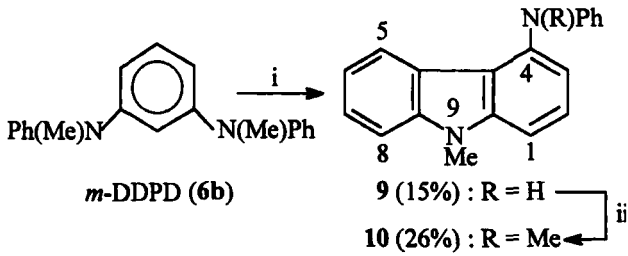


Fig. 1 : HMBC correlations of **9**



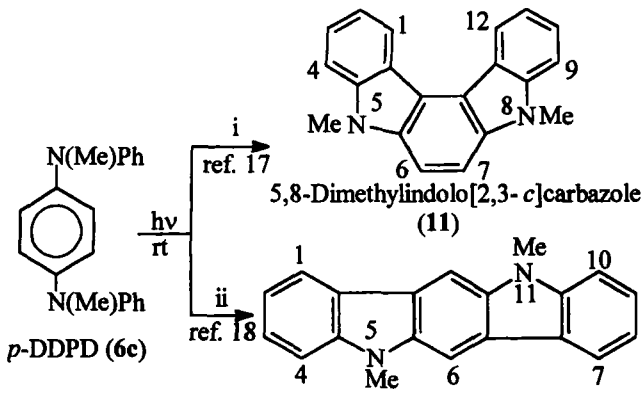
(i) : hν, petroleum ether, rt, 3.5 hr

(ii) : CH_2O, HOAc, $NaBH_3CN$, CH_3CN, rt, 2.5 hr

Scheme 5

The major product was, therefore, expected to be the 4-(*N*-methylanilino) analogue **10**. The identity was confirmed by the reductive methylation of **9** using the cyanoborohydride reagent, which furnished **10** as the sole product (Scheme 5).

The photocyclisation of *para*-DDPD (**6c**) is known[17] to form 5,8-dimethylindolo-[2,3-*c*]carbazole (**11**) which had earlier been erroneously identified[18] as 5,11-dimethylindolo[3,2-*b*]carbazole (**12**) (Scheme 6).



(i) : $CH_3C_6H_{11}$, O_2, 5 hr; 30%

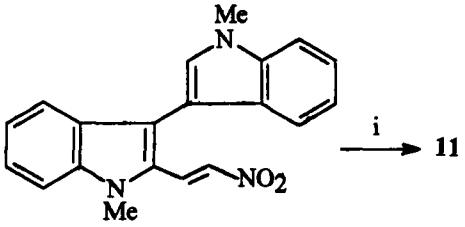
(ii) : C_6H_{14} or Et_2O, 2 hr; 10%

Scheme 6

We had recently noted[19] that the UV irradiation of an ethereal solution of 9-methyl-3-(*N*-methylanilino)carbazole (**13**) furnished the same IC which is formed by the photocyclisation of **6c**. Since the ^{1}H NMR spectral data of the product from **13** could not differentiate between the two possible isomers, **11** and **12**, our identification of the product as **12** had to be based only on the apparent similarity in its UV absorption maxima with those reported[20] for the parent indolo[3,2-*b*]-carbazole (2xNH in place of 2xNMe in **12**) (Scheme 6).

Very recently, the thermal cyclisation of 1,1'-dimethyl-2-(2-nitroethenyl)-3,3'-biindolyl (**14**) has been reported[21] to furnish the angular IC **11** (Scheme 7).

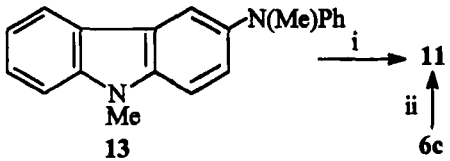
A comparison of the m.p., IR and ^{1}H NMR spectral data of our product[19] with those reported[21] for **11** now leads us to conclude that our photocyclisation product



14

(i) : Ph_2O, 160°, 3 hr; 58%

Scheme 7



(i) : Et_2O, hν, air, rt, 8 hr; 51% (ref. 19)

(ii) : Et_2O + MeOH, hν, rt, 11 hr; 22%

Scheme 8

was indeed the angular isomer **11**, and not **12**. Our previously reported work[19] can, therefore, be revised to as shown in Scheme 8.

The formation of indolo[2,3-*c*]carbazole (**11**) as a result of photocyclisation of **13** invalidates the previous claim[22] that the indolo[2,3-*c*]carbazole nucleus is unlikely to be formed because of the steric crowding of the two terminal benzene nuclei in the angular framework.

In summary, the bis-cyclodehydrogenation of *N,N'*-diphenylphenylenediamines (DPDs) by both palladium(II) acetate and UV light separately succeeded only in the case of *meta*-DPD (**2b**), leading to the formation of indolo[3,2-*a*]carbazole (**5**).

In the case of the corresponding *N,N'*-dimethyl derivatives (DDPDs), only photocyclisation proved to be effective. Bis-cyclisation took place only for *para*-DDPD (**6c**), furnishing 5,8-dimethyl-indolo[2,3-*c*]carbazole (**11**) as the only product. In the case of *ortho*- and *meta*-DDPDs (**6a** and **6b**), monocyclisations with cleavage and retention, respectively of one *N*-methylanilino group occurred, affording the carbazoles **8** from **6a** and **10** from **6b**. The des-methyl derivative **9** was formed as a minor product from **6b**. Additionally, the structure of the product of photocyclisation of 3-(*N*-methylanilino)-9-methylcarbazole (**13**), reported earlier, has been revised to the angular IC **11**.

Finally, since each of **6b** and **6c** was prepared by the condensation of two different aryl nuclei, the methods reported herein can be utilised for the preparation of unsymmetrically substituted indolo[2,3-*b*]- and indolo[2,3-*c*]carbazoles.

Experimental

M.p.s (C), determined on a Toshniwal apparatus, are uncorrected. The UV spectra (λ_{max}, nm) were recorded on Shimadzu UV-160 and UV-240 spectrophotometers, the IR spectra (KBr; ν_{max}, cm^{-1}) on Shimadzu IR-408 and Perkin Elmer IR-782 spectrophotometers. ^1H NMR spectra (δ, ppm) were recorded in $CDCl_3$ using TMS as internal standard on Varian EM-390 (90 MHz), JEOL FX-100 (100 MHz) and Bruker AC-200 (200 MHz) spectrometers and ^{13}C NMR spectra on a Bruker AC-200 (50 MHz) spectrometer. The ^1H, ^{13}C, ^1H-^1H COSY, ^1H-^{13}C one-bond COSY and NOE Spectra of **9** were recorded on a Varian VXR-300 and its HMBC correlations on a Varian XL-400 spectrometer. Electron-impact mass spectra (70 eV) were recorded on a Hitachi RMU-62 mass spectrometer. Photoreactions were carried out using SAIC 400 Watt medium pressure (pyrex filter) and LQ 16 Watt

low pressure (quartz filter) mercury lamps of M/s. Applied Photophysics, U.K. Microanalyses were performed at the Microanalytical Laboratory, Department of Pure Chemistry, University of Calcutta, Calcutta. Column chromatographies (CC) were performed over silica gel (60-120 mesh; Qualigens, India) and thin layer chromatgraphies (TLC) on silica gel G (E. Merck, India) plates. Petrol refers to petroleum ether, b.p. 60-80°. The yields are rounded off to the nearest integers.

Preparation of N,N'-diacetyl-PDs (1a-c). General procedure: Acetic anhydride (19 ml, 0.2 mol) was added dropwise with stirring to an ice-cold solution of the PD (10.8 g, 0.1 mol) in pyridine (10 ml). The solution was left overnight at rt, diluted with benzene (75 ml), the resulting precipitate collected by filtration under suction.

1a (18.8 g, 98%): m.p. 188° (Lit.[23a] 188.5°); IR: 3225 (NH), 1670 (amide CO); **1b** (18.35 g, 96%): m.p. 188-189° (EtOH) (Lit.[23b] 191°); IR: 3300 (NH), 1660 (amide CO); **1c** (18.82 g, 98%): m.p. 310° (Lit.[23a] 310°); IR: 3300 (NH), 1668 (amide CO).

Preparation of DPDs (2a-c). General procedure : A mixture of the diacetyl-PD (1.92 g, 10 mmol), fused K_2CO_3 (10 mmol), Cu-bronze (or Cu_2I_2, 50 mmol) and distilled bromobenzene (5.3 ml, 50 mmol) was refluxed under nitrogen for 25 hr. Excess PhBr was then distilled off at reduced pressure and the residue leached with hot acetone (3x15 ml). The gummy residue from the acetone extract was refluxed with 20% aq. ethanolic KOH (20 ml) for 4.5 hr, diluted with water (20 ml), alcohol boiled off and the cooled reaction mixture poured into brine (100 ml).

It was extracted with ether (2x50 ml), and the residue from the dried ethereal extract was purified by CC. For each DPD, the yields within parenthesis refer to those obtained by using Cu-bronze and Cu(II)-iodide, respectively.

***o*-DPD (2a)** (1.61g, 62%; 2.0g, 77%): Eluted in petrol-EtOAc (10:1); colourless prisms, m.p. 108-109° (MeOH) (Lit.[23c] 109°); IR: 3380 (NH); MS: *m/z* 260 (M^+, 100%), 259, 183, 182, 181, 167, 130 (M^{++}), 77.

***m*-DPD (2b)** (1.46g, 56%; 1.92g, 74%): Eluted in petrol-EtOAc (19:1); m.p. 95-96° (petrol-C_6H_6) (Lit.[23c] 95°); IR: 3355 (NH); δ_H (100 MHz) 5.65 (2H, br, s, D_2O exchangeable, 2xNH), 6.56-7.60 (14H, m, Ar-H); MS: *m/z* 260 (M^+, 100%), 259 (16), 183, 167 (55), 166 (19), 130 (M^{++}, 29).

***p*-DPD (2c)** (0.78g, 30%; 1.55g, 60%): Eluted in petrol-EtOAc (22:3); m.p. 150° (petrol-$CHCl_3$) (Lit.[23d] 152°); IR: 3380 (NH) ; MS: *m /z* 260 (M^+, 100%), 183 (23), 167 (16), 77 (18).

***N*-Phenyl-*m*-PD (3)** (0.53g, 20%; 0.18g, 7%): Eluted in petrol-EtOAc (17:3); brown solid, m.p. 56-58° (petrol-C_6H_6) (Lit.[24] 76-77°) ; IR: 3350 (NH); δ_H (90 MHz) 3.4 (2H, br s) and 5.57 (1H, br, both D_2O exchangeable, NH_2 & NH), 6.22-6.60 (4H, m) and 6.63-7.43 (6H, m, Ar-H + C*H*Cl_3).

Cyclodehydrogenation of *meta*-DPD (2b) (i) Using $Pd(OAc)_2$: A solution of **2b** (0.26 g, 1 mmol) and $Pd(OAc)_2$ (0.45 g, 2 mmol) in gl. acetic acid (5 ml) was refluxed under nitrogen for 1 hr, cooled, diluted with water (50 ml) and neutralised with solid Na_2CO_3. The resulting solid was filtered, washed free of alkali and leached with hot methanol (5x15 ml). The residue obtained from the methanol extract was purified by CC to furnish **5** in petrol-EtOAc (9:1) eluates as white fine crystals (0.04 g, 16%).

Indolo[3,2-*a*]carbazole (5) : m.p. 298-299° (petrol-$CHCl_3$) (Lit.[10] 299-300°); UV: 206, 240, 263, 279, 301, 320, 339, 354; IR: 3313, 3365 (NH); δ_H (200 MHz) 6.95 (1H), 7.07-7.16 (4H + C*H*Cl_3), 7.20-7.34 (2H), 7.42-7.70 (3H) (all m, Ar-H + 2xNH), 8.20 (2H, dd, *J* 8.4, 1.3 Hz; H-1,8); δ_C (50 MHz; DEPT 135) 117.7, 118.9, 121.1, 122.5, 128.6, 129.4, 130.2, 133.5 (all CH), 117.3, 129.7, 141.0, 143.3, 144.9, 165.6 (all C); MS: *m/z* 256 (M^+, 100%), 255 (31), 128 (M^{++}, 19).

(ii) Using photocyclisation : A solution of **2b** (0.2 g, 0.76 mmol) in dry MeOH (350 ml) containing powdered iodine (0.01 g) was irradiated for 40 hr by a 16 Watt mercury lamp and the solution evaporated to residue which was purified by CC to give **5** (0.02 g, 10%).

Reductive methylation of DPDs. General procedure: $NaBH_3CN$ (0.4 g, 7.5 mmol) was added in portions with stirring to a solution of the DPD (**2a-c**) (0.65 g, 2.5 mmol) in CH_3CN (20 ml) containing 37% aq. CH_2O (5 ml). Acetic acid

(0.5 ml) was then added dropwise to the reaction mixture with stirring at rt and the stirring continued for 2.5 hr. It was diluted with water (20 ml), CH_3CN distilled off and the residue extracted with CH_2Cl_2 (3x30 ml). The organic layer was washed, dried (Na_2SO_4) and evaporated to residue which was purified by CC or PTLC.

Products (6a, 7) from *o*-DPD : Two products, Rf 0.44 and 0.30 in petrol-C_6H_6 (19:1), were formed, which were separated by PTLC in the same solvent.

***o*-DDPD (6a)** (0.28 g, 39%) : m.p. 50-51°; (Found: C, 82.90; H, 6.97; N, 9.70. Calc. for $C_{20}H_{20}N_2$: C, 83.33; H, 6.94; N, 9.72%); δ_H (90 MHz) 3.03 (6H, s, 2 x NMe), 6.60 (6H, m) and 7.07-7.40 (8H, m, both Ar-H). ***N*-Methyl-*o*-DDPD (7)** (0.39 g, 57%) : m.p. 63-65° (Found: C, 82.91; H, 6.53; N, 10.21. Calc. for $C_{19}H_{18}N_2$: C, 83.21; H, 6.57; N, 10.22%); δ_H (90 MHz) 3.23 (3H, s, NMe), 6.26 (1H, br s, NH) and 6.70-7.60 (14H, m, Ar-H); MS: *m/z* 274 (M^+, 100%), 273, 259, 258, 197, 195, 182, 181, 180, 167, 77. ***m*-DDPD (6b)** (0.43 g, 60%) : Eluted in petrol-C_6H_6 (9:1); m.p. 54° (petrol); (Found: C, 83.01; H, 6.93; N, 9.75. Calc. for $C_{20}H_{20}N_2$: C, 83.33; H, 6.94; N, 9.72%); δ_H (90 MHz) 3.26 (6H, s, 2 x NMe), 6.48-6.76 (3H, m), 6.80-7.12 (5H, m) and 7.12-7.44 (6H, m, all Ar-H). ***p*-DDPD (6c)** (0.7 g, 97%) : Eluted in petrol-C_6H_6 (9:1); m.p. 153-154° (petrol-CH_2Cl_2) (Lit.[17] 158.3-158.7°; yield 5% from *p*-DPD using $HC(OEt)_3$); δ_H (90 MHz) 3.33 (6H, s, 2 x NMe), 6.83-7.13 (10H, m) and 7.16-7.46 (4H, m, all Ar-H).

Attempted photocyclisation of DDPDs. General procedure : A soln. of the substrate **(6a-c)** (0.2 g, 0.7 mmol) in appropriate solvent (200 ml) was irradiated

using a 400 Watt mercury lamp till the completion of the reaction (TLC). The solvent was then distilled off and the residue purified by CC.

Product from 6a. *N*-Methylcarbazole (8) (0.052 g, 41%) : Obtained by irradiation in Et_2O for 11 hr; eluted in petrol; colourless crystals, m.p. 88° (petrol) (Lit.[25] 88°); δ_H (100 MHz) 3.80 (3H, s, N-CH_3), 7.08-7.64 (6H, m, H-2-7), 8.10 (2H, d, *J* 8.5 Hz, H-1,8); MS: *m/z* 181 (M^+, 100%), 180, 166, 152, 77.

Products from 6b : The irradiation of **6b** in petrol for 3.5 hr furnished a mixture of **9** and **10** which were separated by CC.

9-Methyl-4-(*N*-methylanilino)carbazole (10) (52 mg, 26%) : Eluted in petrol-C_6H_6 (19:1); colourless crystals, m.p. 92° (petrol-C_6H_6); (Found: C, 83.82; H, 6.32; N, 9.83. Calc. for $C_{20}H_{18}N_2$: C, 83.91; H, 6.29; N, 9.79%); δ_H (100 MHz) 3.44, 3.78 (3H, s each, 2xN*Me*Ph), 6.84-7.82 (4H, m), 7.20-7.56 (6H, m), 7.92-8.12 (2H, m, all Ar-H); MS: *m/z* 286 (M^+), 181, 165, 164, 106, 105, 78, 77.

4-Anilino-9-methylcarbazole (9) (28 mg, 15%): Eluted in petrol-C_6H_6 (9:1); colourless crystals; m.p. 202° (petrol-C_6H_6); (Found: C, 83.66; H, 5.83; N, 10.26. Calc. for $C_{19}H_{16}N_2$: C, 83.8; H, 5.88; N, 10.29%); IR: 3375 (NH); δ_H (400 MHz) 3.87 (3H, s, NMe), 6.19 (1H, br s, NH), 6.95 (1H, tt, *J* 7.5, 1 Hz, H-4'), *ca.* 7.10 (2H, dd, *J* 7.5, 1 Hz, H-1,3), 7.12 (2H, dd, *J* 8.5, 1 Hz, H-2',6'), 7.19 (1H, ddd,

J 8, 7, 1 Hz, H-6), 7.30 (2H, dd, *J* 8.5, 7.5 Hz, H-3',5'), 7.40 (1H, t, *J* 7.5 Hz, H-2), 7.41 (1H, dd, *J* 7, 1 Hz, H-8), 7.47 (1H, td, *J* 7, 1 Hz, H-7), 7.99 (1H, dd, *J* 8, 1 Hz, H-5); δ_C (75 MHz) 29.2 (NMe), 102.5 & 109.0 (CH-1,3), 108.1 (CH-8), 117.9 (CH-2',6'), 118.9 (CH-6), 120.8 (CH-4'), 121.9 (CH-5), 124.8 (CH-7), 126.3 (CH-2), 129.3 (CH-3',5'), 114.2 (C-4a), 121.8 (C-4b), 138.8 (C-4), 140.6 (C-8a), 142.5 (C-9a), 143.7 (C-1'); MS: *m/z* 272 (M^+, 100%), 256, 180, 168, 136 (M^{++}), 77.

The irradiation of **6b** (0.2 g) in petrol (250 ml) for 14.5 hr using a 16 Watt mercury lamp furnished, after CC, **10** (34 mg, 17%) and **9** (11 mg, 6%) which were identified by co-TLC, m.p. and m.m.p. determinations with samples from the 400 Watt lot.

5,18-Dimethylindolo[2,3-*c*]carbazole (11) (44 mg, 22%) : Product from **6c** by irradiation in Et_2O (+ little MeOH) for 11 hr; eluted in petrol-C_6H_6 (9:1); m.p. 251-252° (petrol-CH_2Cl_2) (Lit.[17]257.6-258.2°; [19]250-252°; [21]240-244°); UV (λmax reported[17] for **11** within parentheses): 220 (223), 263 (262), 270 (272), 287 (286), 320 (308), 332 (332), 347 (347), 380 (379), (393), 400 (401); identified by co-TLC, m.p., m.m.p. and superimposable IR spectra with a synthetic sample.[19]

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