Thermal Reactions of *N*-Alkyl-2-benzylaniline and *N*-Alkyl-*N*'-phenyl-*o*-phenylenediamine: An Unusual Route to 2-Phenylindole and 2-Phenylbenzimidazole

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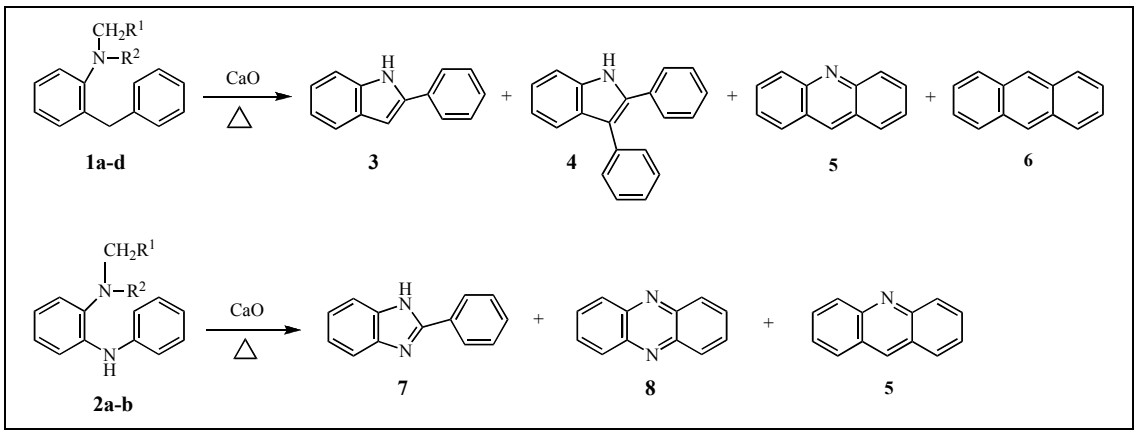

Thermal cyclization reactions of *N*-alkyl-2-benzylaniline **1a-d** and *N*-alkyl-*N*'-phenyl-*o*-phenylenediamine **2a-b** were carried out expecting to get seven-membered heterocyclic compounds. However, the results show that aside from the formation of the normally expected six-membered ring products of acridine **5**, anthracene **6**, and phenazine **8**, thermal cyclization of *N*-alkyl-2-benzylaniline and *N*-alkyl-*N*'-phenyl-*o*-phenylenediamine also resulted to the unexpected formation of 2-phenylindole **3** and 2,3-diphenylindole **4**, and 2-phenylbenzimidazole **7**, respectively.

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INTRODUCTION

Thermal decomposition reactions of *N*-alkyl-2-aminobiphenyls were investigated by passing vapors of the aromatic amines over calcium oxide at 450°C – 600°C. The procedure afforded a method for the preparation of carbazole (69%) and phenanthridine (92%) [1]. Hence, thermal decomposition reactions may also be utilized for the syntheses of other *N*-containing heterocycles which are of great importance in the field of medicine [2] and some areas in material science [3].

A survey of the literature showed many improved methods for the syntheses of indoles and benzimidazoles [4,5] but none describes a method for the synthesis *via* thermal cyclization of *N*-alkyl-2-benzylaniline and *N*-alkyl-*N*'-phenyl-*o*-phenylenediamine in the presence of calcium oxide catalyst.

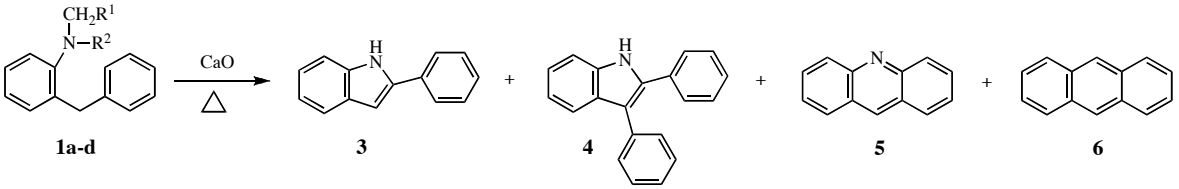
Thus, this paper reports the unusual behavior of *N*-alkyl-2-benzylaniline **1a-d** and *N*-alkyl-*N*'-phenyl-*o*-phenylenediamine **2a-b** when subjected to very high temperatures in the presence of calcium oxide catalyst. The mechanism for the indole and benzimidazole formation by thermal cyclization is also discussed here.

RESULTS AND DISCUSSION

The different substrates (**1a-d** and **2a-b**) for the thermal reactions were synthesized either by methylation or benzylation of 2-benzylaniline and *N*-phenyl-*o*-phenylenediamine. The thermal reactions were carried out at 450°C, 500°C, and 560°C.

The thermally-induced reaction of *N*-methyl-2-benzylaniline **1a** yielded 45% of 2-phenylindole **3** at 450°C (Table 1, Entry1) but decreased as the temperature of the reaction was raised. The reaction also produced acridine **5** and anthracene **6** whose yields remained practically unaffected by the changes in the reaction temperatures (Entry 1, 2, 3). When subjected to very high temperatures, *N*,*N*-dimethyl-2-benzylaniline **1b** also gave 2-phenylindole **3** together with the expected acridine **5** and anthracene **6** (Entry 4, 5, 6). However, the yield of 2-phenylindole **3** is lower compared to that from *N*-methyl-2-benzylaniline **1a** at the same temperature. This can be explained by proposing an imine intermediate in the formation of 2-phenylindole from **1a** and **1b** (Scheme 2). The nitrogen proton of *N*-methyl-2-benzylaniline **1a** is more readily abstracted (more acidic) by calcium oxide

Scheme 1



1a-d **3** **4** **5** **6**

1	R^1	R^2
a	H	H
b	H	CH_3
c	Ph	H
d	Ph	CH_2Ph

Table 1

Thermal cyclization[a] of *N*-alkyl-2-benzylaniline **1a-d**

Entry	Starting material[b]	R^1	R^2	Reaction temperature (°C)	Reaction time[c] (minutes)	Conversion (%)	Product Yield[d] (%)			
							3	**4**	**5**	**6**
1	1a	H	H	450	40	100	45	-	19	10
2	1a	H	H	500	40	100	36	-	19	12
3	1a	H	H	560	40	100	10	-	16	12
4	1b	H	CH_3	450	40	100	36	-	3	10
5	1b	H	CH_3	500	40	100	31	-	4	13
6	1b	H	CH_3	560	40	100	11	-	1	12
7	1c	Ph	H	450	40	100	15	7	69	-
8	1c	Ph	H	500	40	100	4	7	51	-
9	1c	Ph	H	560	40	100	3	6	41	-
10	1d	Ph	CH_2Ph	450	40	100	47	18	26	-
11	1d	Ph	CH_2Ph	500	40	100	26	22	20	-
12	1d	Ph	CH_2Ph	560	40	100	5	14	18	-

[a] Nitrogen carrier gas at 19mL/minute; [b] 1.0 mmol; [c] The reaction time corresponds to the time in minutes for the traveling furnace to reach the stationary furnace (see Experimental Section); [d] Based on reacted starting material.

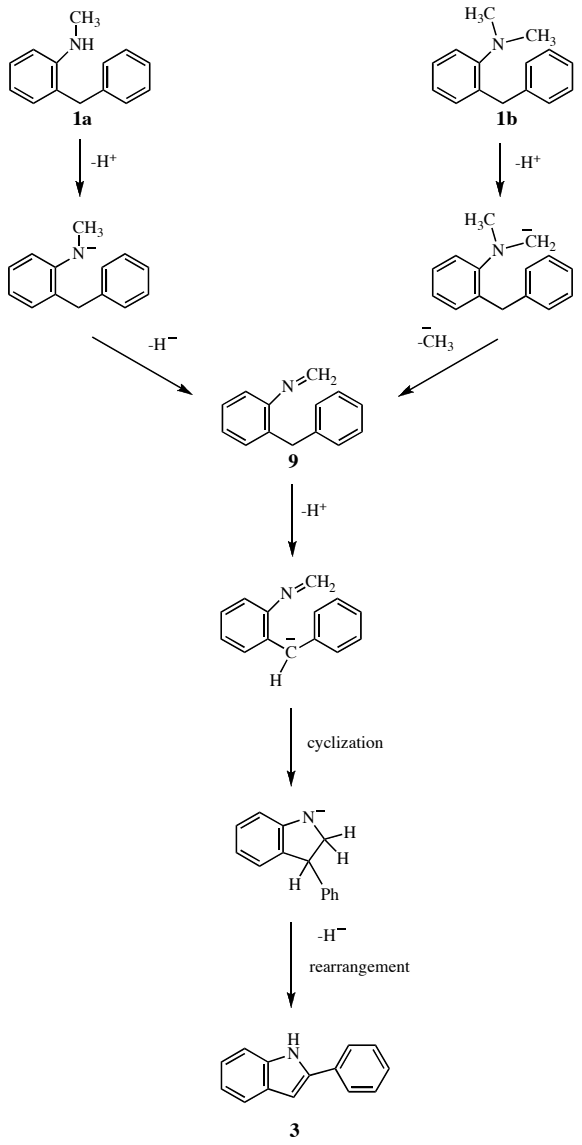
than the methyl proton of *N,N*-dimethyl-2-benzylaniline **1b**, hence a more facile formation of the imine intermediate.

When *N*-benzyl-2-benzylaniline **1c** was heated in the presence of calcium oxide, acridine **5** was produced as the major product, with a yield of 69% at 450°C (Entry 7) but decreased as the reaction temperature was raised due to decomposition. The yield of 2-phenylindole **3** is relatively low at all temperatures (Entry 7, 8, 9).

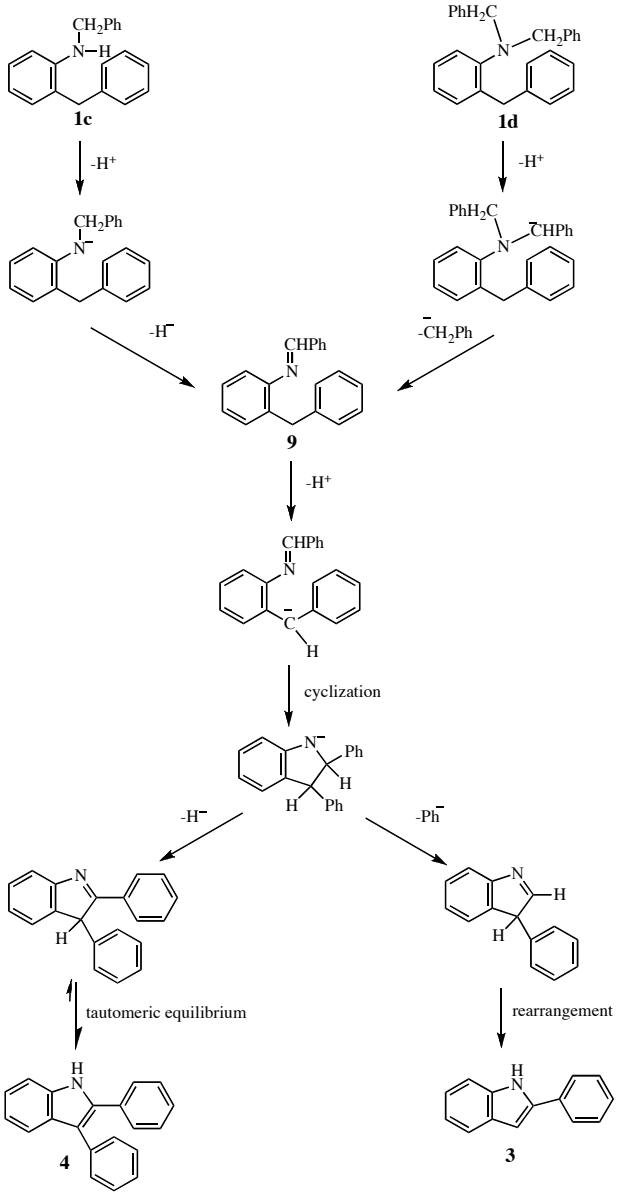
Here, acidity of the nitrogen proton coupled with the facile cleavage of the N-C bond of the benzylamino group at high temperatures made cyclization to form acridine **5** a favored reaction over the formation of the imine intermediate. *N,N*-Dibenzyl-2-benzylaniline **1d**, on the other hand, produced a good yield of 2-phenylindole **3** at 450°C (47%, Entry 10), which decreased as the temperature of the reaction was raised. Abstraction of the methylene proton of one benzyl group followed by facile cleavage of the N-C bond of the second benzyl group led to the formation of an imine intermediate (Scheme 3). The reaction also produced a fair amount of acridine **5** at the three reaction temperatures. It was also observed that *N*-benzyl-2-benzylaniline **1c** and *N,N*-dibenzyl-2-benzylaniline **1d** yielded 2,3-diphenylindole **4**, with *N,N*-dibenzyl-2-benzylaniline **1d** giving a fair yield over *N*-benzyl-2-benzylaniline **1c**.

Thermal reactions of *N,N*-dimethyl-*N'*-phenyl-*o*-phenylenediamine **2a** gave fair yields of 2-phenylbenzimidazole **7** at 450°C and 500°C which decreased radically at 560°C (Table 2, Entry 1, 2, 3). This is due to the fact that although imidazoles are thermally stable, they decompose at temperatures higher than 500°C [6]. The formation of 2-phenylbenzimidazole **7** is rather unusual and may be due to an imine intermediate followed by rearrangement after ring closure reaction. The results for *N,N*-dibenzyl-*N'*-phenyl-*o*-phenylenediamine **2b** show good yield for phenazine **8** at 450°C and fair yields for 2-phenylbenzimidazole **7** at 450°C and 500°C (Entry 4, 5). Again, decomposition at 560°C led to a decrease in the yield of 2-phenylbenzimidazole **7** and phenazine **8** (Entry 6). Unexpectedly high yield of phenazine **8** is obtained from *N,N*-dibenzyl-*N'*-phenyl-*o*-phenylenediamine **2b** as

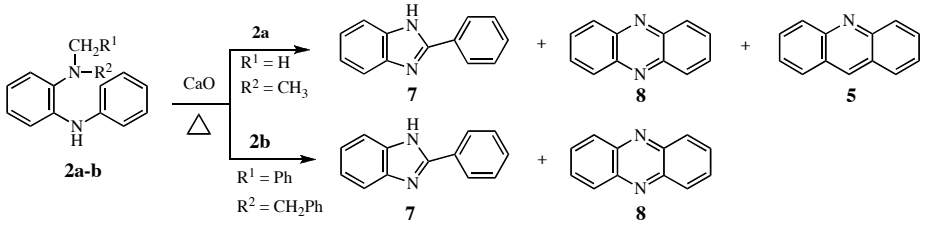
Scheme 2



Scheme 3



Scheme 4



compared with *N,N*-dimethyl-*N*'-phenyl-*o*-phenylenediamine **2a**, due to the facile cleavage of the N-C bond of the benzylamino group which favored the cyclization reaction over the formation of the imine intermediate (Scheme 5) [7].

In another experiment, the proposition that the indole and benzimidazole were formed through an imine intermediate was investigated. *N*-Benzylidene-2-benzylaniline **9** and *N*-benzylidene-*N*'-phenyl-*o*-phenylenediamine were synthesized from 2-benzylaniline and

Table 2

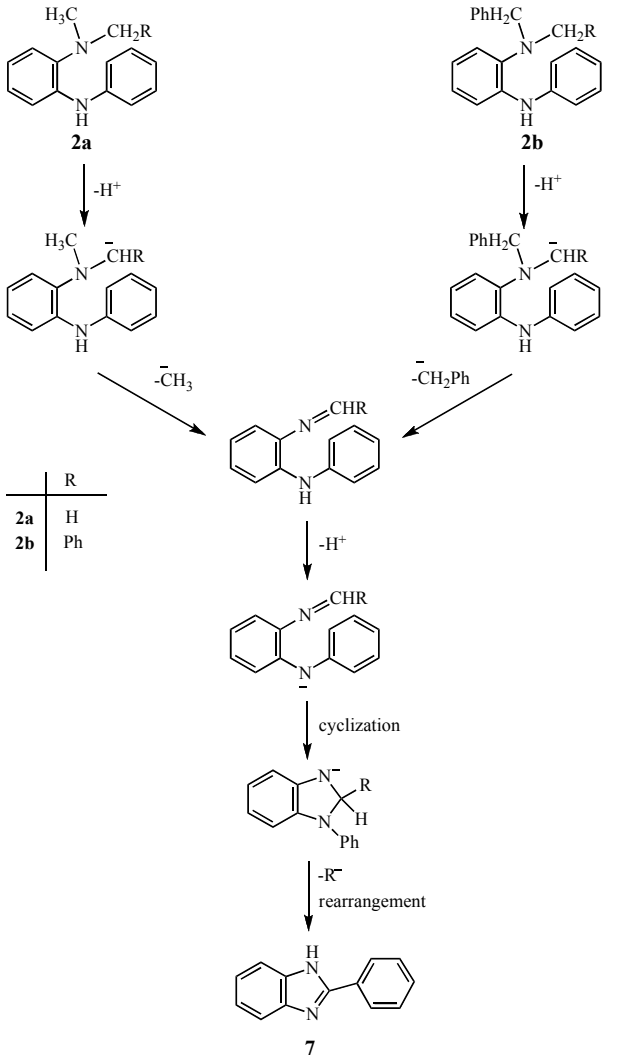
Thermal cyclization[a] of *N*-alky-*N*'-phenyl-*o*-phenylenediamine **2a-b**

Entry	Starting material[b]	R^1	R^2	Reaction temperature (°C)	Reaction time[c] (minutes)	Conversion (%)	Product Yield[d] (%) **7**	**8**	**5**
1	2a	H	CH_3	450	40	100	31	9	11
2	2a	H	CH_3	500	40	100	32	6	11
3	2a	H	CH_3	560	40	100	14	5	6
4	2b	Ph	CH_2Ph	450	40	100	33	52	-
5	2b	Ph	CH_2Ph	500	40	100	37	37	-
6	2b	Ph	CH_2Ph	560	40	100	21	20	-

[a] Nitrogen carrier gas at 19mL/minute; [b] 1.0 mmol; [c] The reaction time corresponds to the time in minutes for the traveling furnace to reach the stationary furnace (see Experimental Section); [d] Based on ^{1}H nmr data.

N-phenyl-*o*-phenylenediamine, respectively. However, the synthesized *N*-benzylidene-*N*'-phenyl-*o*-phenylenediamine reverted back to the original amine during column chromatography. Only *N*-benzylidene-2-benzylaniline **9** was subjected to thermal reactions and the results are given in Table 3.

Scheme 5



The results show that a good yield of 2-phenylindole **3** and 2,3-diphenylindole **4** (Table 3, Entry 1, 2) were obtained from *N*-benzylidene-2-benzylaniline **9**. This proved that the unusual formation of 2-phenylindole **3** occurs *via* an imine intermediate. On the other hand, the mechanism for the formation of benzimidazole *via* an imine intermediate cannot be validated due to the instability of *N*-benzylidene-*N*'-phenyl-*o*-phenylenediamine that was synthesized. Fair amounts of acridine **5** and fluorene **10** were also obtained from the thermal reactions of *N*-benzylidene-2-benzylaniline **9** at the three temperatures (Entry 1, 2, 3).

EXPERIMENTAL

Melting points are uncorrected. Column chromatography was performed on silica gel (Wakogel C-200). Unless otherwise stated, anhydrous sodium sulfate was employed as the drying agent. Ether refers to diethyl ether. The ir spectra were determined on a Hitachi Model 270-30 IR Spectrophotometer. The ^{1}H and ^{13}C nmr spectra were determined at 500 MHz and 125 MHz, respectively, on a Varian Unity plus-500W NMR Spectrophotometer, using tetramethylsilane as the internal standard.

General Procedure for Thermolysis Reaction [8] of *N*-Alkyl-2-benzylaniline 1a-d and *N*-Alkyl-*N*'-phenyl-*o*-phenylenediamine 2a-b. Elemental analysis apparatus (Micro Elemental Analyzer, Mitamura Riken Kogyo Inc.) was used for the thermolysis reaction. Granules of calcium oxide were obtained by grinding large pieces of calcium oxide (Nakalai Tesque, Inc.) and collecting particles which passed through the 5 mm sieve and retained by the 2 mm sieve. A quartz tube (66 cm in length, 12 mm i.d.) was packed to a length of 28 cm with the calcium oxide granules (18.0 g). The tube was positioned in the horizontal stationary furnace with heating coils (38 cm in length). The column was then purged with N_2 gas at a rate of about 19 mL/min and kept at this condition throughout the experiment. The stationary furnace was kept at the reaction temperature (450-600 °C). Starting material (1.0 mmole) was weighed into a quartz boat and placed inside the reaction tube at 3 cm from the stationary furnace and vaporized by the traveling furnace under N_2 carrier gas. When the reaction temperature was 450°C or 500°C, the stationary furnace was kept at 450 °C or 500 °C while the traveling furnace was kept at 560°C. When the reaction temperatures were 560°C and higher (temperature of the stationary furnace), the traveling furnace was raised to reaction temperature plus 50°C. The traveling furnace was set to

Scheme 6

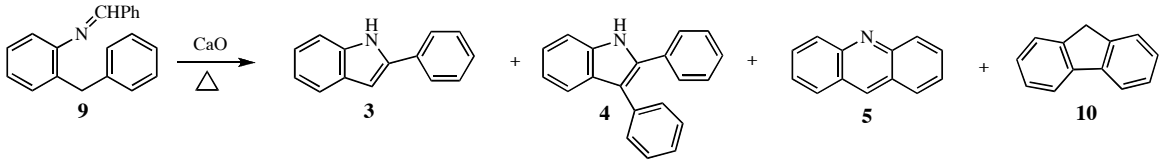


Table 3

Thermal cyclization[a] of *N*-benzylidene-2-benzylaniline **9**

Entry	Starting material[b]	Reaction temperature (°C)	Reaction time[c] (minutes)	Conversion (%)	Product Yield[d] (%)			
					3	**4**	**5**	**10**
1	9	450	40	100	18	39	20	16
2	9	500	40	100	21	15	13	23
3	9	560	40	100	10	0	3	16

[a] Nitrogen carrier gas at 19mL/minute; [b] 1.0 mmol; [c] The reaction time corresponds to the time in minutes for the traveling furnace to reach the stationary furnace (see Experimental Section); [d] Based on reacted starting material.

motion gradually, reached the stationary furnace in 35 minutes and kept for 5 minutes at this state. Products which came from the outlet (5 mm i.d.) of the quartz tube were collected in a vessel cooled with ice-water. The products were extracted with acetone. After removal of the acetone, the residue was chromatographed on a silica gel column and eluted with benzene, benzene-hexane or benzene-ethyl acetate to give a variety of products. Structures of the products were determined from their spectra. Compounds **3**, **5**, **6**, **7**, and **8** were identified by comparison of the ir, ^{1}H nmr and ^{13}C nmr spectra with those of commercially available samples and compound **4** by comparison of its spectral data with literature value.

***N*-Methyl-2-benzylaniline (1a) and *N*,*N*-Dimethyl-2-benzylaniline (1b).** 2 *M* Sodium hydroxide solution (5 mL) was added to a mixture of 2-benzylaniline (0.71 g, 3.87 mmol) and water (10 mL). To the mixture, dimethylsulfoxide (1.36 mL, 11 mmol) was added and the mixture was stirred for 3 hours at room temperature. When the solution became acidic, 2 *M* sodium hydroxide was added to keep it basic. After reaction, the mixture was extracted with ether. The extract was washed, dried over sodium sulfate and evaporated. The product was chromatographed on a silica gel column and eluted with benzene:hexane (4:1) to give *N*-methyl-2-benzylaniline **1a** (0.159 g, 21%, colorless crystals from ethanol, mp 39-40°C) and *N*,*N*-dimethyl-2-benzylaniline **1b** (0.397g, 49%, colorless oil) [9].

***N*-Methyl-2-benzylaniline (1a).** ir(KBr): 3436 cm^{-1} (NH); ^{1}H nmr (deuteriochloroform): δ 2.75 (s, 3H, CH_3), 3.52 (broad s, 1H, NH), 3.86 (s, 2H, CH_2), 6.64 (d, J=7.5 Hz, 1H, Ar-H), 6.72 (dd, J=7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.02 (d, J=7.5 Hz, 1H, Ar-H), 7.16 (d, J=7.5 Hz, 2H, 2 Ar-H), 7.18-7.22 (m, 2H, 2 Ar-H), 7.27 (dd, J=7.5 Hz and 7.5 Hz, 2H, 2 Ar-H); ^{13}C nmr (deuteriochloroform): δ 30.8 (q), 38.0 (t), 110.1 (d), 117.1 (d), 124.6 (d), 126.4 (s), 127.9 (d), 128.5 (d), 128.7 (d), 130.5 (d), 139.4 (s), 147.3 (s). *Anal.* Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.30; H, 7.62; N, 7.22.

***N*,*N*-Dimethyl-2-benzylaniline (1b):** ^{1}H nmr (deuteriochloroform): δ 2.66 (s, 6H, 2 CH_3), 4.10 (s, 2H, CH_2), 6.96 (dd, J=7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.02 (d, J=7.5 Hz, 1H, Ar-H), 7.13 (d, J=7.5 Hz, 1H, Ar-H), 7.15-7.19 (m, 4H, 4 Ar-H), 7.18 (d, J=7.5 Hz, 2H, 2 Ar-H), 7.25 (dd, J=7.5 Hz and 7.5 Hz, 2H, 2 Ar-H); ^{13}C nmr (deuteriochloroform): δ 36.6 (t), 45.2 (q), 119.5 (d), 123.4 (d), 125.8 (d), 126.9 (d), 128.3 (d), 129.2 (d), 130.9 (d), 135.9 (s), 141.8 (s), 152.9 (s). *Anal.* Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.14; H, 8.04; N, 6.72.

***N*-Benzyl-2-benzylaniline (1c).** 2-Benzylaniline (1.632 g, 8.91 mmol), benzaldehyde (4.74 mL, 44.6 mmol), sodium acetate trihydrate (3.80 g, 26.76 mmol) and acetic acid (7.5 mL, 128.4 mmol) were added to ethanol (20 mL). The mixture was stirred for 30 minutes at room temperature. To the solution, sodium borohydride (1.65 g, 44.6 mmol) was added under cooling with ice-water and the solution was stirred for another 30 minutes. 2 *M* Sodium hydroxide solution was then added until alkaline and the solution was extracted with ether. The extract was washed, dried over sodium sulfate and evaporated. The product was chromatographed on a silica gel column and eluted with benzene:hexane (4:1) to give *N*-benzyl-2-benzylaniline **1c** (1.893 g, 78%, crystals) [10]. Recrystallization from ethanol gave colorless crystals, mp 38-40°C; ir(KBr): 3432 cm^{-1} (NH); ^{1}H nmr (deuteriochloroform): δ 3.90 (s, 2H, CH_2), 4.23 (s, 2H, CH_2-N), 6.61 (d, J=7.5 Hz, 1H, Ar-H), 6.71 (dd, J=7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.06-7.28 (m, 13H, 12 Ar-H, 1 NH); ^{13}C nmr (deuteriochloroform): δ 38.3 (t), 48.0 (t), 110.9 (d), 117.3 (d), 124.7 (s), 126.5 (d), 127.1 (d), 127.2 (d), 127.9 (d), 128.5 (d), 128.6 (d), 128.7 (d), 130.7 (d), 139.3 (s), 139.4 (s), 145.9 (s). *Anal.* Calcd for $C_{20}H_{19}N$: C, 87.87; H, 7.01; N, 5.12. Found: C, 87.96; H, 7.02; N, 5.22.

***N*,*N*-Dibenzyl-2-benzylaniline (1d).** 2-Benzylaniline (0.30 g, 1.64 mmol), benzyl bromide (0.40 mL, 3.36 mmol) and potassium carbonate (0.464g, 3.36 mmol) were added to dimethylsulfoxide (10 mL). The mixture was stirred for 2.5 hours at room temperature. The mixture was then extracted with ether. The extract was washed, dried over sodium sulfate and evaporated. The product was chromatographed on a silica gel column and eluted with benzene:hexane (4:1) to give *N*,*N*-dibenzyl-2-benzylaniline **1d** (0.551g, 91%, colorless oil) [11]; ^{1}H nmr (deuteriochloroform): δ 4.05 (s, 4H, 2 NH_2Ph), 4.18 (s, 2H, CH_2Ph), 6.96 (d, J=7.5 Hz, 1H, Ar-H), 7.05-7.28 (m, 18H, 18 Ar-H); ^{13}C nmr (deuteriochloroform): δ 36.5 (t), 57.9 (t),

123.3 (d), 124.2 (d), 125.8 (d), 126.5 (d), 126.9 (d), 128.1 (d), 128.3 (d), 128.9 (d), 129.2 (d), 130.9 (d), 137.4 (s), 138.3 (s), 141.5 (s), 149.6 (s). *Anal.* Calcd for $C_{27}H_{25}N$: C, 89.21; H, 6.93; N, 3.85. Found: C, 89.34; H, 6.82; N, 3.94.

***N,N*-Dimethyl-*N*'-phenyl-*o*-phenylenediamine** (**2a**). *N*-Phenyl-*o*-phenylenediamine (1.14 g, 6.19 mmol), methyl iodide (1.20 mL, 18.57 mmol) and tripotassium phosphate (0.03 g, 0.14 mmol) were added to dimethylsulfoxide (20 mL). The mixture was kept at 60°C for 1 hour with constant stirring. When the mixture became acidic, tripotassium phosphate (0.01g, 0.05 mmol) was added. The product was extracted with ether. The extract was washed, dried over sodium sulfate and evaporated. The product was chromatographed on a silica gel column and eluted with benzene:hexane (4:1) to give *N,N*-dimethyl-*N*'-phenyl-*o*-phenylenediamine **2a** (1.093 g, 83%, colorless oil) [12]; ir(neat): 3368 cm^{-1} (NH); ^{1}H nmr (deuteriochloroform): δ 2.66 (s, 6H, 2 CH_3), 6.56 (s, 1H, NH), 6.84 (dd, J= 7.5 Hz and 7.5 Hz, 1H, Ar-H), 6.90 (dd, J=7.5 Hz and 7.5 Hz, 1H, Ar-H), 6.97 (dd, J=7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.08 (d, J= 7.5 Hz, 1H, Ar-H), 7.14 (d, J=7.5 Hz, 2H, 2 Ar-H), 7.26 (dd, J=7.5 Hz and 7.5 Hz, 2H, 2 Ar-H), 7.31 (d, J=7.5 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 44.0 (q), 114.3 (d), 118.1 (d), 119.7 (d), 119.9 (d), 120.8 (d), 124.0 (d), 129.1 (d), 137.9 (s), 142.3 (s), 142.8 (s). *Anal.* Calcd for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20. Found: C, 79.12; H, 7.72; N, 13.34.

***N,N*-Dibenzyl-*N*'-phenyl-*o*-phenylenediamine** (**2b**). *N*-Phenyl-*o*-phenylenediamine (0.10 g, 0.55 mmol), benzyl bromide (0.13 mL, 1.1 mmol) and potassium carbonate (0.152 g, 1.1 mmol) were added to dimethylsulfoxide (10 mL). The mixture was stirred for 2.5 hours at room temperature. The mixture was then extracted with ether. The extract was washed, dried over sodium sulfate and evaporated. The product was chromatographed on a silica gel column and eluted with hexane:ethyl acetate (3:1) to give *N, N*-dibenzyl-*N*'-phenyl-*o*-phenylenediamine **2b** (0.082 g, 41%, colorless oil) [13]; ir(neat): 3380 cm^{-1} (NH); ^{1}H nmr (deuteriochloroform): δ 4.05 (s, 4H, 2 $PhCH_2$), 6.76 (dd, J=7.5 Hz and 7.5 Hz, 1H, A-H), 6.84 (s, 1H, NH), 6.92 (dd, J=7.5 Hz and 7.5 Hz, 1H, Ar-H), 6.97 (dd, J=7.5 Hz and 7.5 Hz, 1H, Ar-H), 7.03 (d, J=7.5 Hz, 1H, Ar-H), 7.06 (d, J=7.5 Hz, 2H, 2 Ar-H), 7.18-7.28 (m, 13H, 13 Ar-H); ^{13}C nmr (deuteriochloroform): δ 57.3 (t), 114.3 (d), 118.7 (d), 119.4 (d), 121.1 (d), 123.6 (d), 124.9 (d), 127.1 (d), 128.2 (d), 128.9 (d), 129.2 (d), 137.9 (s), 138.7 (s), 139.3 (s), 142.8 (s). *Anal.* Calcd for $C_{26}H_{24}N_2$: C, 85.68; H, 6.64; N, 7.69. Found: C, 85.54; H, 6.68; N, 7.80.

2-Phenylindole (**3**). mp (ethanol) 187-188 °C; ir(KBr): 3444 cm^{-1} (NH); ^{1}H nmr (deuteriochloroform): δ 6.83 (s, 1H, indole C-H), 7.12 (dd, J=8.0 Hz and 8.0 Hz, 1H, Ar-H), 7.20 (dd, J=8.0 Hz and 8.0 Hz, 1H, Ar-H), 7.32 (dd, J=8.0 Hz and 8.0 Hz, 1H, Ar-H), 7.40 (d, J=8.0 Hz, 1H, Ar-H), 7.45 (dd, J=8.0 Hz and 8.0 Hz, 2H, 2 Ar-H), 7.63 (d, J=8.0 Hz, 1H, Ar-H), 7.67 (d, J=8.0 Hz, 2H, 2 Ar-H), 8.33 (broad s, 1H, NH); ^{13}C nmr (deuteriochloroform): δ 100.0 (d), 110.9 (d), 120.2 (d), 120.6 (d), 122.3 (d), 125.1 (d), 127.7 (d), 129.0 (d), 129.2 (s), 132.3 (s), 136.8 (s), 137.9 (s).

2,3-Diphenylindole (**4**). mp (ethanol) 120-123°C (lit. [13] mp 122-124°C); ir(KBr): 3400 cm^{-1} (NH); ^{1}H nmr (deuteriochloroform): δ 7.15 (dd, J=7.5 Hz and 7.5 Hz, 1H, 1 Ar-H), 7.25 (dd, J=7.5 Hz and 7.5 Hz, 1H, 1 Ar-H), 7.29 (dd, J=7.5 Hz and 7.5 Hz, 1H, 1 Ar-H), 7.31 (dd, J=7.5 Hz and 7.5 Hz, 1H, 1 Ar-H), 7.33 (dd, J=7.5 Hz and 7.5 Hz, 2H, 2 Ar-H), 7.38 (dd, J=7.5 Hz and 7.5 Hz, 2H, 2 Ar-H), 7.42 – 7.46 (m, 5H, 5 Ar-H), 7.68 (d, J=7.5 Hz, 1H, 1 Ar-H), 8.23 (s, 1H, NH); ^{13}C nmr (deuteriochloroform) [13]: δ 110.9 (d), 115.0 (s), 119.7 (d), 120.4 (d), 122.7 (d), 126.2 (d), 127.7 (d), 128.2 (s), 128.5 (d), 128.7 (d), 128.7 (d), 130.1 (d), 132.7 (s), 134.1 (s), 135.0 (s), 135.9 (s). Spectral properties are identical with those in the literature [14].

2-Phenylbenzimidazole (**7**). mp (benzene) 290-291°C; ir(KBr): 3050 cm^{-1} (NH); ^{1}H nmr (deuteriochloroform): δ 7.26-7.30 (m, 2H, 2 Ar-H), 7.46-7.50 (m,, 3H, 3 Ar-H), 7.65 (broad s, 1H, NH), 7.65-7.67 (m, 2H, 2 Ar-H), 8.07 (d, J=9.0 Hz, 1H, Ar-H); ^{13}C nmr (deuteriodimethylsulfoxide): δ 111.3 (d), 118.9 (d), 122.1 (d), 122.1 (d) 126.6 (d), 128.6 (d), 129.7 (d), 130.2 (s), 135.1 (s), 143.7 (s), 151.2 (s).

***N*-Benzylidene-2-benzylaniline** (**9**). 2-Benzylaniline (0.366g, 2 mmol) and benzaldehyde (0.106g, 1 mmol) were added to benzene (20 mL). The mixture was heated to 40°C for 2 hours under constant stirring. The mixture was then extracted with ether. The extract was washed, dried over anhydrous sodium sulfate and evaporated. The product was chromatographed on a silica gel column and eluted with hexane:ethyl acetate (5:1) to give 55% *N*-benzylidene-2-benzyl-aniline **9** as a colorless oil. ir(neat): 1620 cm^{-1} (C=N); ^{1}H nmr (deuteriochloroform): δ 4.15 (s, 2H, CH_2), 6.97 (d, J=7.5 Hz, 1H, Ar-H), 7.12-7.26 (m, 8H, 8 Ar-H), 7.46-7.49 (m, 3H, 3 Ar-H), 7.88-7.90 (m, 2H, 2 Ar-H), 8.32 (s, 1H, N=C-H); ^{13}C nmr (deuteriochloroform): δ 37.4 (t), 117.8 (d), 125.7 (d), 125.9 (d), 127.3 (d), 128.2 (d), 128.7 (d), 128.7 (d), 129.0 (d), 129.9 (d), 131.2 (d), 135.1 (s), 136.4 (s), 141.4 (s), 150.5 (s), 159.7 (d).

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