Thermal Decomposition Reactions of *N*-Alkylated 2-Aminobiphenyls to Carbazole and Phenanthridine

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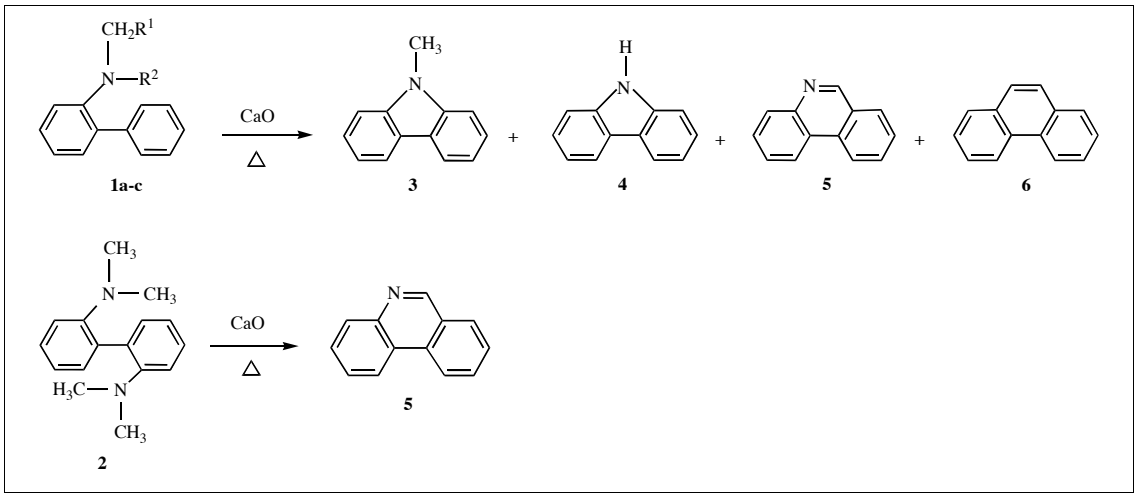

Thermal cyclization reactions were examined by passing vapors of *N*-alkylated 2-aminobiphenyls **1a-c** and **2** over calcium oxide at 450-600°C under nitrogen carrier gas. The reactions yielded 9-methylcarbazole **3**, carbazole **4**, phenanthridine **5** and phenanthrene **6**. The major product for the reactions of **1a**, **1b** and **2** was phenanthridine **5** while that of **1c** was carbazole **4**.

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Introduction.

Nitrogen-containing heterocycles such as carbazole are important compounds due to their biological activities [1] as well as in electroactive and related areas in material science [2]. These heterocycles may be synthesized by a variety of methods and for carbazole, three methods of synthesis by intramolecular cyclization have been reported: (a) reaction of 2-nitrobiphenyl with triethyl phosphite [3] or iron (II) oxalate [4], (b) thermal and photochemical decomposition of 2-azidobiphenyl [5], and (c) dehydrogenation of 2-aminobiphenyl over metal oxide at high temperature [6]. The dehydrogenation was used to synthesize 4*H*-benzo[*def*]carbazole [7]. In the previous paper [8], we reported that dehydrogenation of aromatic amines by calcium oxide is a powerful method to prepare five- and six-membered heterocycles such as carbazole, acridine, phenazine and 4*H*-benzo[*def*]carbazole from 2-aminobiphenyl, 2-aminodiphenylmethane, 2-aminodi-phenylamine and 4-aminophenanthrene.

In this paper, we report the intramolecular cyclization of *N*-alkylated 2-aminobiphenyls **1a-c** and **2**. Methyl and benzyl groups were selected as alkyl substituents on the amino group, from the viewpoints of facile synthesis and easy elimination of proton from both methyl and benzylic carbon atoms.

Results and Discussion.

For the intramolecular cyclization reactions, *N*-alkylated 2-aminobiphenyls **1a-c** were prepared by methylation or benzylation of 2-aminobiphenyl. Similarly, compound **2** was synthesized by methylation of 2,2'-diaminobiphenyl. 9-Benzylcarbazole **7** was prepared by benzylation of carbazole while 9-methylcarbazole **3** is commercially available.

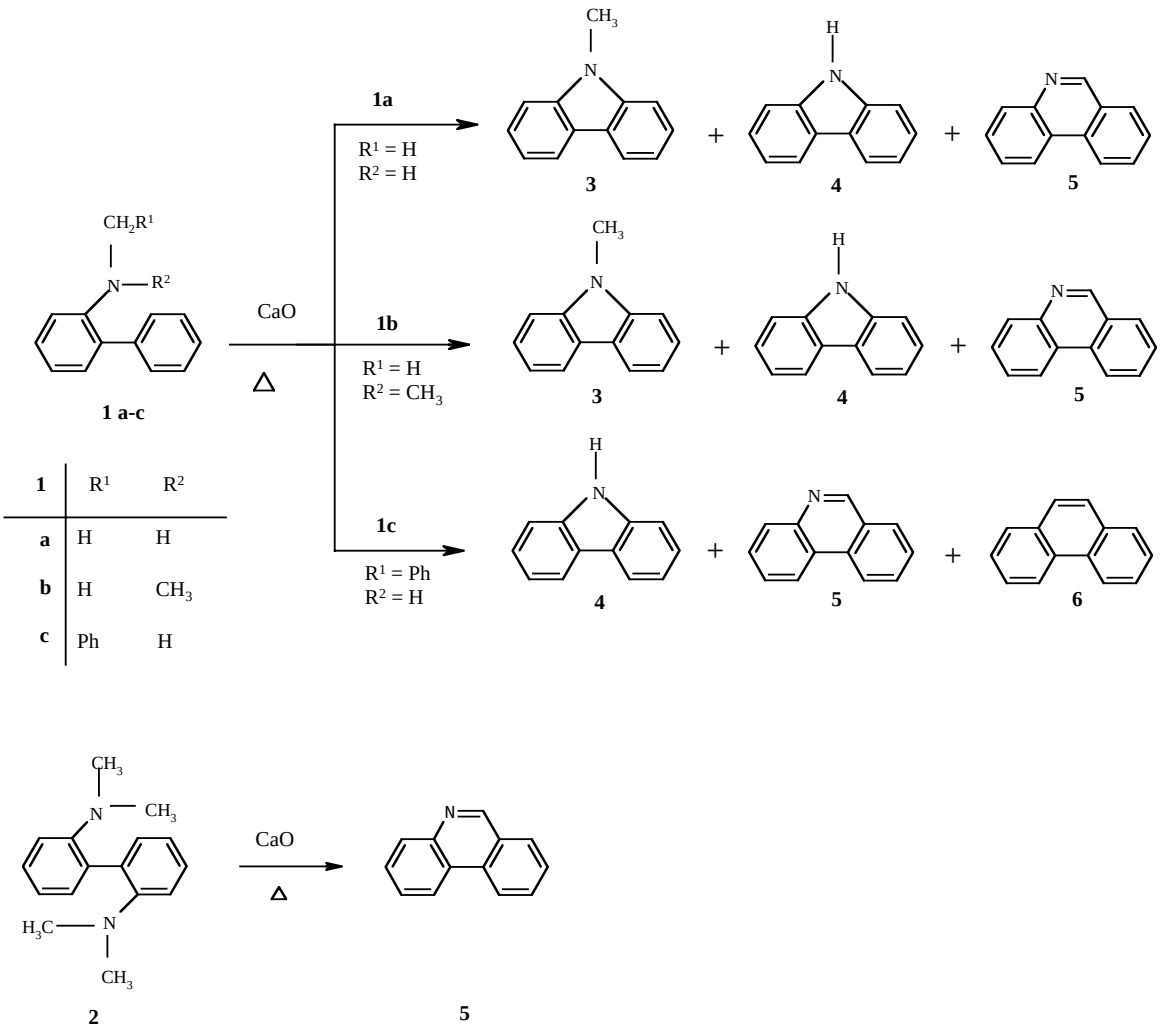
The starting material was placed in a quartz boat, vaporized with a traveling furnace and introduced by nitrogen carrier gas to the stationary furnace containing the calcium oxide which was heated at the reaction temperature. The detailed general procedure and diagram of the apparatus used for the intramolecular cyclization of

N-alkylated aromatic amines are described in the Experimental Section.

Initially, cyclization reactions of *N*-alkylated 2-aminobiphenyls **1a-c** and **2** were examined at the temperature range of 450-600°C. The results are summarized in Table 1.

When 2-methylaminobiphenyl **1a** (R^1 = H, R^2 = H) was heated over calcium oxide at 500°C, five-membered 9-methylcarbazole **3** (19%) and carbazole **4** (25%), and six-membered phenanthridine **5** (38%) were obtained at the conversion of 100% (Entry 1). In the formation of **5**, the methyl group of **1a** was incorporated in the cyclization step. Raising the temperature to 600°C decreased the yields of each product (0, 13, and 15%, respectively) because of decomposition (Entry 3). Thus, in the thermal cyclization reactions of 2-methylaminobiphenyl **1a**, ring-expanded phenanthridine **5** was obtained as a major product. For the 2-dimethylaminobiphenyl **1b** (R^1 = H, R^2 = CH_3) which possesses no amino hydrogen, the reaction at 500°C yielded 60% phenanthridine **5** along with carbazole **4** (15%) and 9-methylcarbazole **3** (3%) (Entry 4). Increasing the reaction temperature to 600°C reduced the yield of phenanthridine **5** (33%) due to decomposition (Entry 6). To examine substituent effect on the cyclization step, 2, 2'-bis(dimethylamino)biphenyl **2** was subjected to thermal reaction. At

Scheme 1



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

450°C, **2** afforded only phenanthridine **5** in 92% yield (Entry 10). This fact suggests that carbanion formed through deprotonation from one dimethylamino group attacks selectively a benzene-ring carbon substituted by the second dimethylamino group because of the presence of a leaving group. Raising the temperature to 500 and 560°C decreased the yields (80, 64%) of **5** because of decomposition (Entry 11, 12). When 2-benzylaminobiphenyl **1c** (R^1 = Ph, R^2 = H) was treated at 500°C, carbazole **4** (69%), phenanthridine **5** (5%),

Table 1

Thermal decomposition reaction[a] of *N*-alkylated 2-aminobiphenyl derivatives **1a-c**, **2**

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	500	40	100	19	25	38	0
2	**1a**	H	H	560	40	100	0	25	32	0
3	**1a**	H	H	600	40	100	0	13	15	0
4	**1b**	H	CH_3	500	40	100	3	15	60	0
5	**1b**	H	CH_3	560	40	100	0	17	58	0
6	**1b**	H	CH_3	600	40	100	0	14	33	0
7	**1c**	Ph	H	500	40	100	0	69	5	12
8	**1c**	Ph	H	560	40	100	0	57	4	11
9	**1c**	Ph	H	600	40	100	0	26	4	5
10	**2**	-	-	450	40	100	0	0	92	0
11	**2**	-	-	500	40	100	0	0	80	0
12	**2**	-	-	560	40	100	0	0	64	0

[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.

and phenanthrene **6** (12%) were obtained (Entry 7). Reaction at 560°C gave similar results to those at 500°C (Entry 7, 8), while the reaction at 600 °C gave lower yields (Entry 9) due to decomposition. In this case, carbazole **4** was the major product and ring-expanded phenanthridine **5** was a minor product. The results suggest facile fission of the bond between nitrogen atom and the benzyl group.

To examine the reaction pathways of cyclization, 9-methylcarbazole **3** and 9-benzylcarbazole **7** were subjected to similar reaction conditions (Table 2). When **3** was heated at 500°C, carbazole **4** and phenanthridine **5** were produced in 36 and 46% yields, respectively (Entry 1). Reaction at 560°C gave similar results while the reaction at 600°C decreased the yield of both **4** and **5** (21, 24%, respectively) (Entry 3). The results show that carbazole **4** and phenanthridine **5** are produced *via* 9-methylcarbazole [9], which is one of the reaction pathways. When 9-benzylcarbazole **7** was treated at 500°C, carbazole **4** (64%), phenanthridine **5** (20%), and phenanthrene **6** (13%) were obtained (Entry 4). In this case, elimination of the benzyl group was a major reaction and yielded phenanthrene. Raising the temperature to 560 and 600°C caused a decrease in the yields of each compound **4**, **5**, and **6** (Entry 5, 6). These results show that the thermal cyclization reaction of *N*-alkylated 2-aminobiphenyls **1a-c** and **2** afforded the ring-expanded phenanthridine **5**.

In conclusion, thermal cycization of *N*-alkylated 2-aminobiphenyls afforded carbazole and ring-expanded phenanthridine.

EXPERIMENTAL

The 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 ^1H and ^{13}C

Scheme 2

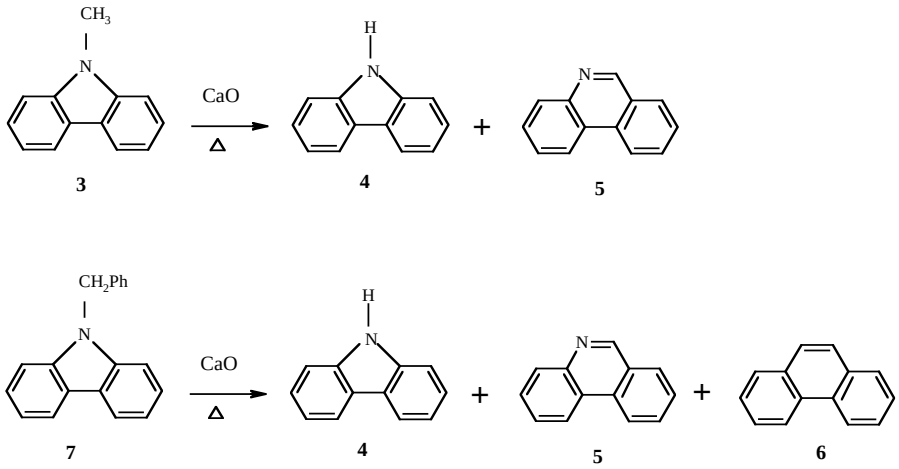


Table 2
Thermal decomposition reaction[a] of 9-methyl- and 9-benzylcarbazoles **3**, **7**

Entry	Starting material[b]	R	Reaction temperature (°C)	Reaction Time[c] (minutes)	Conversion (%)	Product Yield[d] (%) **4**	**5**	**6**
1	**3**	CH_3	500	40	95	36	46	0
2	**3**	CH_3	560	40	100	37	43	0
3	**3**	CH_3	600	40	100	21	24	0
4	**7**	CH_2Ph	500	40	100	64	20	13
5	**7**	CH_2Ph	560	40	100	52	11	9
6	**7**	CH_2Ph	600	40	100	33	6	5

[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.

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 of Aromatic Amines **1a-c** and **2**.

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 600°C (temperatures of the stationary furnace), the traveling furnace was raised to reaction temperature plus 50°C. The traveling furnace was set to 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 silica gel 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**, **4**, **5**, and **6** were identified by comparison of the ir, ^{1}H nmr and ^{13}C nmr spectra with those of commercially available samples.

Themolysis Reaction of 2-Methylaminobiphenyl at 500°C.

The quartz tube was packed with calcium oxide granules to a length of 28 cm and placed horizontally in the furnace (Figure 1). The apparatus was then purged with nitrogen gas at a rate of 19 mL/min and kept at this condition throughout the experiment. The stationary furnace was heated to 500°C while the traveling furnace was heated to 560°C. 2-Methylaminobiphenyl (0.201 g, 1.10 mmole) was weighed into the quartz boat and positioned at 3 cm from the stationary furnace. The traveling furnace was gradually set to motion until it reached the stationary furnace, which took 35 minutes, and was kept at this state for 5 minutes more. The products which came out of the reaction tube were collected in ice-cooled vessels and extracted with acetone. The tlc profile of the acetone extract was taken using benzene:hexane (1:4) as the mobile phase. The plate showed three distinct spots under an ultraviolet light (254 nm). The R_f values of the spots were 0.33, 0.10 and 0.03. Authentic samples of carbazole, 9-methylcarbzole, phenanthridine, as well as 2-methylamino-biphenyl were also spotted on the same plate with the acetone extract and gave R_f values of 0.10, 0.34, 0.03, and 0.20, respectively. The acetone was then evaporated and the residue chromatographed on a silica gel column and eluted with benzene:hexane (1:4), benzene, and ethyl acetate. The tlc profile of the different fractions collected were determined using benzene:hexane (1:4) as the mobile phase. Fractions with the same tlc profile were pooled together and the solvent evaporated. The first compound eluted had an R_f of 0.33 (9-methylcarbazole) and weighed 37 mg (19% yield) while the second compound had an R_f of 0.10 (carbazole) and weighed 46 mg (25% yield). The last compound eluted had an R_f of 0.03 (phenanthridine) and weighed 75 mg (38% yield). The structures of the products were determined by comparison of their ir, ^{1}H nmr and ^{13}C nmr spectra with commercially available samples of the compounds.

9-Methylcarbazole (**3**): mp 86-87°C; ^{1}H nmr (deuterio-chloroform): δ 3.81 (s, 3H, CH_3), 7.22 (dd, J = 8.5 and 8.5 Hz, 2H, 2 Ar-H), 7.37 (d, J = 8.5 Hz, 2H, 2 Ar-H), 7.46 (dd, J = 8.5 and 8.5 Hz, 2H, 2 Ar-H), 8.08 (d, J = 8.5 Hz, 2H, 2 Ar-H); ^{13}C nmr (deutriochloroform): δ 28.7 (q), 108.1 (d), 118.5 (d), 120.0 (d), 122.5 (s), 125.4 (d), 140.7 (s).

Anal. Calcd. for $C_{13}H_{11}N$: C, 86.16; H, 6.18; N, 7.73. Found: C, 86.02; H, 6.28; N, 7.52.

Carbazole (**4**): mp 243-245°C; ir (potassium bromide): 3450 cm^{-1} (NH); ^{1}H nmr (deuterioacetone): δ 7.17 (dd, J = 8.0 and 8.0 Hz, 2H, 2 Ar-H), 7.39 (dd, 8.0 and 8.0 Hz, 2H, 2 Ar-H), 7.51 (d, J = 8.0 Hz, 2H, 2 Ar-H), 8.11 (d, J = 8.0 Hz, 2H, 2 Ar-H), 10.32 (broad s, 1H, NH); ^{13}C nmr (deuterioacetone): δ 111.6 (d), 119.6 (d), 120.8 (d), 123.9 (s), 126.3 (d), 140.9 (s).

Anal. Calcd. for $C_{12}H_9N$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.38; H, 5.36; N, 8.50.

Phenanthridine (**5**): mp 105-106°C; ^{1}H nmr (deuterio-chloroform): δ 7.26-7.77 (m, 3H, 3 Ar-H), 7.88 (dd, J = 7.0 and 7.0 Hz, 1H, Ar-H), 8.06 (d, J = 8.0 Hz, 1H, Ar-H), 8.21 (d, J = 7.0 Hz, 1H, Ar-H), 8.59 (d, J = 8.0 Hz, 1H, Ar-H), 8.62 (d, J =

8.0 Hz, 1H, Ar-H), 9.30 (s, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 121.8 (d),122.2 (d), 124.1 (s), 126.3 (s), 127.0 (d), 127.4 (d), 128.6 (d), 128.7 (d), 130.1 (d), 131.0 (d), 132.5 (s), 144.4 (s), 153.5 (d).

Anal. Calcd. for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.28; H, 4.94; N, 7.72.

2-Methylaminobiphenyl (**1a**) and 2-Dimethylaminobiphenyl (**1b**).

2-Aminobiphenyl (4.25 g, 25.1 mmol), dimethyl sulfate (9.31 g, 73.8 mmol) and 2 *M* sodium hydroxide solution (20 mL) were added to water (60 mL). The mixture was stirred for 5 hours at room temperature. During the reaction, the alkalinity of the solution was monitored and 2 *M* sodium hydroxide solution (5 mL) was added to ensure that the solution is basic. The resulting mixture was extracted with ether. The ether extract was washed, dried and evaporated. The residue was chromatographed on a silica gel column and eluted with benzene-hexane (4:1) to give **1a** (1.37 g, 30%) as a colorless oil and **1b** (1.72 g, 35%) as a colorless oil [13].

1a: ir (neat): 3460 cm^{-1} (NH); ^{1}H nmr (deuteriochloroform): δ 2.79 (s, 3H, CH_3), 3.99 (broad s, 1H, NH), 6.69 (d, J=7.5 Hz, 1H, Ar-H), 6.77 (dd, J=7.5 and 7.5 Hz, 1H, Ar-H), 7.09 (d, J=7.5 Hz, 1H, Ar-H), 7.27 (dd, J=7.5 and 7.5 Hz, 1H, Ar-H), 7.34 (dd, J=7.5 and 7.5 Hz, 1H, Ar-H), 7.39-7.45 (m, 4H, 4 Ar-H); ^{13}C nmr (deuteriochloroform): δ 30.8 (q), 109.8 (d), 116.8 (d), 127.2 (d), 127.6 (s), 128.8 (d), 128.9 (d), 129.4 (d), 130.0 (d), 139.5 (s), 146.1 (s).

Anal. Calcd for $C_{13}H_{13}N$: C, 85.20; H, 7.15; N, 7.64. Found: C, 85.38; H, 7.09; N, 7.50.

1b: ^{1}H nmr (deuteriochloroform): δ 2.54 (s, 6H, 2 CH_3), 6.99-7.04 (m, 2H, 2 Ar-H), 7.22 (d, J=7.5 Hz, 1H, Ar-H), 7.25-7.30 (m, 2H, 2 Ar-H), 7.39 (dd, J=7.5 and 7.5 Hz, 2H, 2 Ar-H), 7.57 (d, J=7.5 Hz, 2H, 2 Ar-H). ^{13}C nmr (deuteriochloroform): δ 43.3 (q), 117.5 (d), 121.4 (d), 126.4 (d), 128.0 (d), 128.3 (d), 128.6 (d), 131.7 (d), 134.1 (s), 142.0 (s), 151.2 (s).

Anal. Calcd for $C_{14}H_{15}N$: C, 85.23; H, 7.66; N, 7.10. Found: C, 85.12; H, 7.76; N, 7.18.

2-Benzylaminobiphenyl (**1c**).

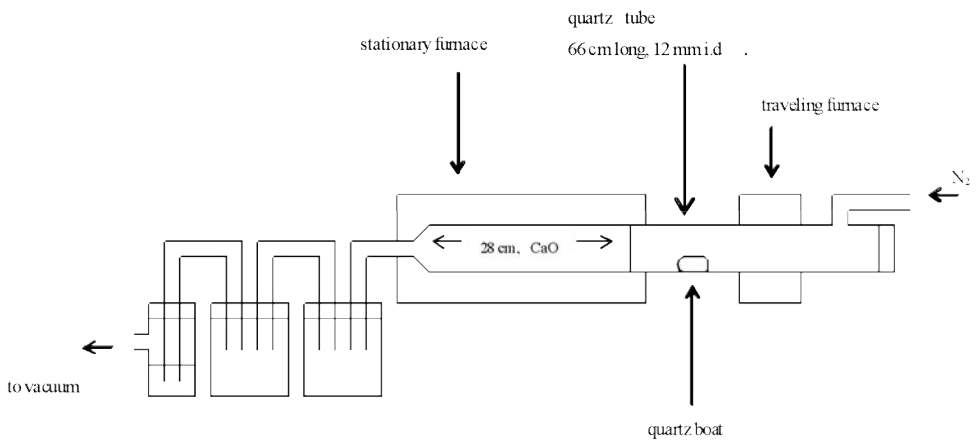
Compound **1c** was prepared according to the procedure by Schellenberg [14]. 2-Aminobiphenyl (1.70 g, 10.0 mmol) was dissolved in ethanol (20 mL). To the solution, benzaldehyde (5.23 g, 49.3 mmol), sodium acetate trihydrate (2.70 g, 19.8 mmol) and acetic acid (8.81 g, 147 mmol) were added. After cooling the solution in the ice-water bath, sodium borohydride (2.00 g, 53.0 mmol) was added gradually and the solution was stirred for 10 minutes. The solution was made alkaline by adding 2 *M* sodium hydroxide solution. The resulting solution was then extracted with ether. The ether extract was washed, dried and evaporated. The product was recrystallized from benzene-hexane to give **1c** (1.76 g, 68%) as colorless crystals, mp 88-89°C (lit. [15] mp 89-91°C). ir (potassium bromide): 3440 cm^{-1} (NH);); ^{1}H nmr (deuteriochloroform): δ 4.33 (s, 2H, CH_2), 4.40 (broad s, 1H, NH), 6.65 (d, J=7.5 Hz, 1H, Ar-H), 6.77 (dd, J=7.5 and 7.5 Hz, 1H, Ar-H), 7.11 (d, J=7.5 Hz, 1H, Ar-H), 7.18 (dd, J=7.5 and 7.5 Hz, 1H, Ar-H), 7.21-7.36 (m, 6H, 6 Ar-H), 7.42-7.48 (m, 4H, 4 Ar-H); ^{13}C nmr (deuteriochloroform): δ 48.1 (t), 110.7 (d), 117.1 (d), 127.0 (d), 127.2 (d), 127.6 (s), 128.3 (d), 128.6 (d), 128.7 (d), 128.9 (d), 129.4 (d), 130.2 (d), 139.4 (s), 144.8 (s).

Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 87.82; H, 6.72; N, 5.42.

2,2'-Bis(dimethylamino)biphenyl (**2**).

2,2'-Diaminobiphenyl (0.553 g, 3.00 mmol), methyl iodide (1.82 g, 12.8 mmol), and tripotassium phosphate (1.00 g, 4.72 mmol) were dissolved in dimethylsulfoxide (2.00 mL). The solution was stirred for 1 hour at room temperature. The solution was made basic by adding 2 *M* sodium hydroxide solution (2.0 mL) and extracted with ether. The ether extract was washed, dried and evaporated. The residue was chromatographed and eluted with hexane-ethyl acetate (3:1) to give **2** (0.555 g, 77%). Recrystallization from ethanol gave colorless crystals, mp 68-69°C (lit. [16] mp 69°C). ^{1}H nmr (deuteriochloroform): δ 2.57 (s, 6H, 2 CH_3), 6.96 (dd, J=7.5 and 7.5 Hz, 2H, 2 Ar-H), 7.02 (d, J=7.5 Hz, 2H, 2 Ar-H), 7.23 (dd, J=7.5 and 7.5 Hz, 2H, 2 Ar-H), 7.37 (d, J=7.5 Hz, 2H, 2 Ar-H); ^{13}C nmr (deuteriochloroform): δ 42.9 (q), 118.0 (d), 120.8 (d), 127.5 (d), 131.5 (d), 133.3 (s), 150.3 (s).

Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.95; H, 8.39; N, 11.66. Found: C, 80.16; H, 8.30; N, 11.48.



A schematic representation of the apparatus used for the thermal cyclization of aromatic amines.

Figure 1

9-Benzylcarbazole (**7**).

Carbazole (2.00 g, 12.0 mmol), benzyl bromide (2.30 g, 13.5 mmol) and tripotassium phosphate (6.40 g, 30.2 mmol) were dissolved in dimethylsulfoxide (32 mL). The solution was stirred for 7 hours at 70°C. After removal of insoluble materials by filtration, the solution was poured into water and extracted with ether. The ether extract was washed, dried and evaporated. The residue was chromatographed and eluted with benzene-hexane (1:4) to give **7** (1.63 g, 53%). Recrystallization from benzene-hexane gave colorless crystals, mp 110-111°C (lit. [18] mp 112-113°C). ^{1}H nmr (deuteriochloroform): δ 5.51 (s, 2H, CH_2), 7.14 (d, J=7.5 Hz, 2H, 2 Ar-H), 7.23-7.26 (m, 5H, 5 Ar-H), 7.36 (d, J=7.5 Hz, 2H, 2 Ar-H), 7.43 (dd, J=7.5 and 7.5 Hz, 2H, 2 Ar-H), 8.13 (d, J=7.5 Hz, 2H, 2 Ar-H); ^{13}C nmr (deuteriochloroform): δ 46.5 (t), 108.9 (d), 119.2 (d), 120.4 (d), 123.0 (s), 125.8 (d), 126.4 (d), 127.4 (d), 128.7 (d), 137.2 (s), 140.6 (s).

Anal. Calcd for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.54; H, 5.40; N, 5.51.

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