Synthesis of Carbazole, Acridine, Phenazine, 4*H*-Benzo[*def*]carbazole and Their Derivatives by Thermal Cyclization Reaction of Aromatic Amines

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A variety of nitrogen-containing heterocycles were synthesized by passing vapors of aromatic amines over calcium oxide at 450-650 °C under nitrogen carrier gas. Reaction of 2-aminobiphenyl **3a** at 560 °C gave carbazole **4** in 80% yield. Reaction of 2,2'-diaminobiphenyl **3b** afforded a mixture of carbazole **4** and 4-aminocarbozole **6b**. In the case of 2-amino-2'-nitrobiphenyl **3c**, benzo[*c*]cinnoline **7** was obtained along with carbazole **4**. Reaction of 2-amino-2'-methoxybiphenyl **3d** gave four products of carbazole **4**, 4-hydroxycarbazole **6e**, phenanthridine **8** and dibenzofuran **9**. Reaction of 2-aminodiphenylmethane **5a** afforded acridine **10**. In the case of 2-aminobenzophenone **5b**, acridone **11** was obtained as a major product. Reaction of 2-aminobenzhydrol **5c** gave acridine **10**. When 2-aminodiphenylamine **5d** was reacted, phenazine **12** was obtained in good yield. In contrast, reaction of 2-aminodiphenyl ether **5e** produced only 2-hydroxydiphenylamine **13**. Reaction of 4-aminophenanthrene **14** produced 4*H*-benzo[*def*]carbazole **15** in 61% yield.

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Introduction.

Nitrogen-containing heterocycles are important compounds and synthesized by a variety of methods. A survey of the chemical literature shows that three general procedures have been reported for cyclizing 2-substituted biphenyls **1**-**3** into carbazole **4**. The starting material consist of 2-nitrobiphenyl **1**, 2-azidobiphenyl **2** or 2-aminobiphenyl **3**. The bridging process involves the loss of two oxygen (deoxygenation), two atoms of nitrogen (denitrogenation) or two atoms of hydrogen (dehydrogenation). Waterman and Vivian obtained carbazole **4** in 63% yield by heating 2-nitrobiphenyl **1** with deoxygenating agent such as iron (II) oxalate [1]. More recently, Cadogan and coworkers used triethyl phosphite to abstract the oxygen and gave carbazole **4** in 82% yield [2]. Smith and Brown decomposed 2-azidobiphenyl **2** either thermally or photochemically to give carbazole **4** in *ca*. 77% yield [3]. Swenton and coworkers converted 2-azidobiphenyl **2** photochemically into carbazole **4** in 68-78% yield [4]. The reactions of 2-nitrobiphenyl **1** and 2-azidobiphenyl **2** to carbazole **4** are considered to proceed *via* nitrene intermediates [5]. Morgan and Walls prepared carbazole **4** (42-60%) and phenanthrene (4-6%) by heating 2-aminobiphenyl **3** (R=H) at 500-600 °C with oxidizing agents such as vanadium (V) oxide, molibudenum (VI) oxide or manganese (IV) oxide [6]. Surprisingly, using calcium oxide, magnesium oxide or pumice carbazole was obtained in lower yield (32%) [6]. Weinmayr prepared carbazole **4** by heating 2-aminobiphenyl **3** (R=H) with 1,3-dinitrobenzene at 250-360 °C [7].

These methods have been employed in the synthesis of 4*H*-benzo[*def*]carbazole from 4-substituted phenanthrene. Thus, Kruber and Grigoleit obtained 4*H*-benzo[*def*]carbazole in 20% yield by passing vapors of 4-aminophenanthrene over calcium oxide at 400 °C [8]. We increased the yield to 53% by raising the reaction temperature to 560 °C [9]. Kreher and Koehler converted 4-azidophenanthrene into 4*H*-benzo[*def*]carbazole (66% yield) by thermolysis at 240 °C in diphenyl ether solution [10]. Thus, bridging between nitrogen atom and benzene ring is a convenient method to prepare carbazole derivatives.

In the previous paper [11], we reported synthesis of nitrogen-containing heterocycles such as carbazole **4** (53%), 4*H*-naphtho[1,4-*def*]carbazole (52%) and phenoxazine (18%) by passing aromatic amines dissolved in benzene over calcium oxide at 400-700 °C. We modified the synthetic method of nitrogen-containing heterocycles without solvent and applied to several aromatic amines. In this paper we wish to report the result of cyclization reactions. As starting materials for intramolecular cyclization, 2-amino-2'-substituted biphenyls **3a**-**d**, 2-aminodiphenylmethanes **5a**-**c**, 2-aminodiphenylamine **5d** and 2-aminodiphenyl ether **5e** were used. In the case of 2-aminobiphenyls **3a-d**, amino, nitro and methoxyl groups were introduced as substituents to examine cyclization position on the benzene ring and reaction mechanisms. Compounds

5a-e have one atom (carbon, nitrogen or oxygen) between two benzene rings and are expected to afford six-membered ring heterocycles.

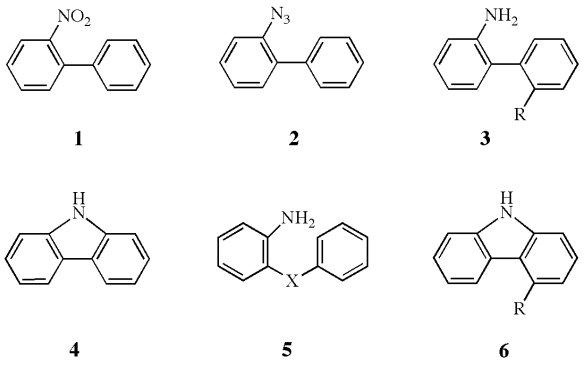


Figure 1

Results and Discussion.

As starting materials for intramolecular cyclization, 2,2'-diaminobiphenyl **3b** (R=NH_2) [12] and 2-amino-2'-nitrobiphenyl **3c** (R=NO_2) [13] were synthesized by reduction of 2,2'-dinitrobiphenyl according to literature. 2-Amino-2-methoxybiphenyl **3d** (R=OCH_3) [14], 2-aminodiphenylmethane **5a** (X=CH_2) [15] and 2-aminobenzhydrol **5c** (X=CHOH) [16] were prepared according to literature. Other starting materials **3a** (R=H), **5b** (X=CO), **5d** (X=NH), **5e** (X=O) are commercially available. The starting material was placed in a quartz column, vaporized with a travelling furnace and introduced by nitrogen carrier gas to calcium oxide, which was heated at reaction temperature with a stationary furnace. Detailed general procedure for intramolecular cyclization of aromatic amines is described in Experimental section.

Initially, intramolecular cyclization reactions of 2-amino-2'-substituted biphenyls **3a-d** (R=H, NH_2, NO_2, OCH_3) were examined at the temperature range of 450-560 °C. The results are summarized in Table 1.

When 2-aminobiphenyl **3a** (R=H) was heated over calcium oxide (Nakalai Tesque, Inc.) at 560 °C, carbazole **4** was obtained in 80% yield at the conversion of 100% (Entry 1). This method is convenient because (a) starting materials are readily available and procedure is simple, (b) yield is better or comparable to those (32-83%) using 2-nitrobiphenyl [1-2], 2-azidobiphenyl [3-4] and 2-aminobiphenyl [6], (c) calcium oxide is very cheap and harmless, (d) reaction time is short and solvent is not needed.

Next, 2'-substituted biphenyls **3b-d** reacted to examine cyclization position on the benzene ring. On reaction of 2,2'-diaminobiphenyl **3b** at 560 °C, a mixture of carbazole **4** (24%) and 4-aminocarbazole **6b** (65%) was produced (Entry 3). However, reaction of **3b** at 500 °C lowered the conversion (46%) (Entry 2). The results show that intramolecular cyclization between the amino group and benzene ring occurred in two ways and major product was amino group-containing compound. Reaction of 2-amino-2'-nitrobiphenyl **3c** at 400 °C gave a mixture of carbazole **4** (9%) and benzo[*c*]cinnoline **7** (46%) (Entry 4). In this case, nitro group-containing carbazole **6c** was not produced at all showing good leaving ability of nitro group. Raising the reaction temperature to 560 °C, the product ratio of carbazole **4** (44%) and benzo[*c*]cinnoline **7** (6%) was reverted (Entry 5-7). Benzo[*c*]cinnoline **7** would be formed through dehydration between amino group and nitro group followed by deoxygenation under reductive atmosphere. Benzo[*c*]cinnoline **7** is prepared by reduction of 2,2'-dinitrobiphenyl with bismuth-potassium hydroxide [17] or sodium borohydride. Reaction of 2-amino-2'-

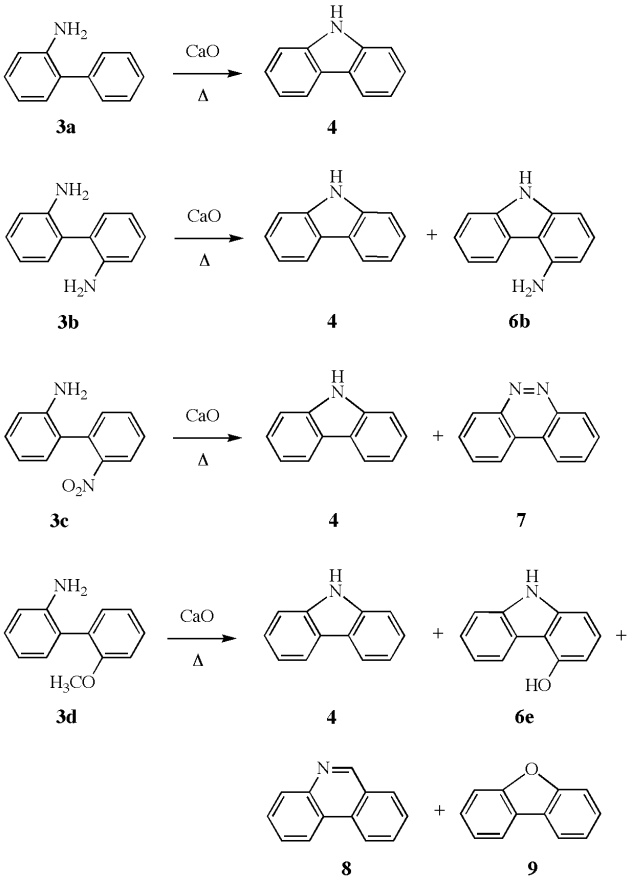
Table 1

Intramolecular Thermal Cyclization of 2-Amino-2'-substituted Biphenyl Derivatives **3a-d** [a]

Entry	Starting material [b]	R	Reaction temperature (°C)	Reaction time[c] (minutes)	Conversion (%)	Product (Yield [d], %)				
						4	**6**	**7**	**8**	**9**
1	**3a**	H	560	40	100	80	-	-	-	-
2	**3b**	NH_2	500	40	46	22	53 [e]	-	-	-
3	**3b**	NH_2	560	40	100	24	65 [e]	-	-	-
4	**3c**	NO_2	400	40	100	9	0 [f]	46	-	-
5	**3c**	NO_2	450	40	100	21	0 [f]	28	-	-
6	**3c**	NO_2	500	40	100	40	0 [f]	8	-	-
7	**3c**	NO_2	560	40	100	44	0 [f]	6	-	-
8	**3d**	OCH_3	450	40	88	27	0 [g]	-	8	7
9	**3d**	OCH_3	500	40	100	22	7 [g]	-	12	20
10	**3d**	OCH_3	560	40	100	17	9 [g]	-	15	27

[a] Nitrogen carrier gas 19 ml / minute; [b] 1.77 Mmoles; [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; [e] Product **6b**; [f] Product **6c**; [g] Product **6e**.

Scheme 1



Scheme 2

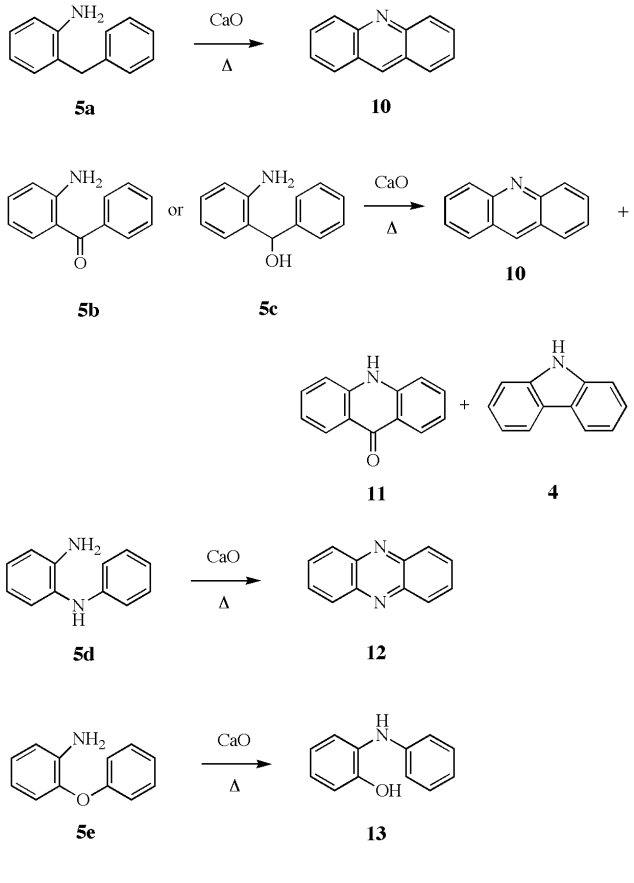


Table 2

Intramolecular Thermal Cyclization of 2-Aminodiphenylmethane Derivatives **5a-c**, 2-Aminodiphenylamine **5d** and 2-Aminodiphenyl ether **5e** [a]

Entry	Starting material [b]	X	Reaction temperature (°C)	Reaction time[c] (minutes)	Conversion (%)	Product (Yield [d], %)				
						10	**11**	**4**	**12**	**13**
1	**5a**	CH_2	500	40	40	58	-	-	-	-
2	**5a**	CH_2	560	40	100	70	-	-	-	-
3	**5a**	CH_2	600	40	100	75	-	-	-	-
4	**5a**	CH_2	650	40	100	64	-	-	-	-
5	**5b**	CO	450	40	96	3	21	2	-	-
6	**5b**	CO	500	40	100	6	27	7	-	-
7	**5b**	CO	560	40	100	6	32	11	-	-
8	**5b**	CO	600	40	100	7	23	14	-	-
9	**5c**	CHOH	450	40	100	12	0	0	-	-
10	**5c**	CHOH	500	40	100	23	0	0	-	-
11	**5c**	CHOH	560	40	100	50	4	0	-	-
12	**5c**	CHOH	600	40	100	31	3	0	-	-
13	**5d**	NH	450	40	35	-	-	-	51	-
14	**5d**	NH	500	40	80	-	-	-	76	-
15	**5d**	NH	560	40	100	-	-	-	76	-
16	**5d**	NH	600	40	100	-	-	-	77	-
17	**5e**	O	450	40	56	-	-	-	-	25
18	**5e**	O	500	40	100	-	-	-	-	0
19	**5e**	O	560	40	100	-	-	-	-	0

[a] Nitrogen carrier gas 19 ml / minute; [b] 1.77 Mmoles; [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.

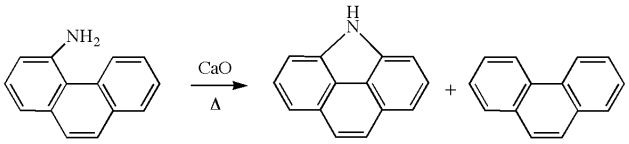
methoxybiphenyl **3d** at 450-560 °C afforded a mixture of carbazoles **4** (17-27%), phenanthridine **8** (8-15%), dibenzofuran **9** (7-27%), and 4-hydroxycarbazole **6e** (0-9%) (Entry 8-10). The result shows that both the nitrogen and oxygen atoms attacked benzene ring to give heterocycles.

Reactions of aromatic amines **5** possesing one atom X (X=CH_2, CO, NH, O) between aminophenyl and phenyl groups were carried out under similar conditions. The results are summarized in Table 2.

When 2-aminodiphenylmethane **5a** (X=CH_2) was reacted over calcium oxide at 500 °C, acridine **10** was obtained in 58% yield at the conversion of 40% (Entry 1). Raising the reaction temperature to 650 °C increased yield (64-75%) at the conversion of 100% (Entry 2-4). The method is useful to synthesize acridine **10** and yield is better than that (11%) from flash vaccum pyrolylis of 2-aminodiphenylmethane [18] and comparable to that (10-95%) from 2-azidodiphenylmethane [19]. Reaction of 2-aminobenzophenone **5b** (X=CO) at 450-600 °C afforded a mixture of acridine **10** (3-7%), acridone **11** (21-32%) and carbazole **4** (2-14%) and yields of each product are not good (Entry 5-8). Similarly, reaction of 2-aminobenzhydrol **5c** at 450-600 °C gave mainly acridine **10** (12-50%) along with small amount of acridone **11** (0-4%) (Entry 9-12). When 2-aminodiphenylamine **5d** was reacted at 450-600 °C, phenazine **12** was obtained in good yields (51-77%) (Entry 13-16). The yield is better compared to flash vaccum pyrolysis (57%) of 2-aminodiphenylamine [20] and reaction (46%) of 2-nitrodiphenylamine with iron [1a]. In contrast, reaction of 2-aminodiphenyl ether **5e** at 450 °C gave only 2-hydroxydiphenylamine **13** in 25% yield and phenazine was not obtained (Entry 17-19).

Finally, results of intramolecular cyclization of 4-aminophenanthrene **14** are summarized in Table 3. 4*H*-Benzo[*def*]carbazole **15** was obtained in 61% yield at the conversion of 98% at 600 °C (Entry 2). The yield is a little better than that (53%) [9] reported early and comparable to that (66%) from 4-azidophenanthrene [10].

Scheme 3



14 **15** **16**

Thus, intramolecular cyclization of aromatic amines over calcium oxide is useful and convenient synthetic method of nitrogen-containing five- and six-membered heterocycles.

Mechanisms of intramolecular cyclization are not clear enough at the present time. In this paper, we propose a little different mechanism from previous one [11]. Plausible reaction mechanisms of **3** are shown in Scheme 4 from substituent effects of amino, methoxyl and nitro groups on cyclization step.

Table 3

Intramolecular Thermal Cyclization of 4-Aminophenanthrene **14** [a]

Entry	Starting material [b]	Reaction temperature (°C)	Reaction time[c] (minutes)	Conversion (%)	Product (Yield [d], %) **15**	**16**
1	**14**	560	40	44	60	12
2	**14**	600	40	98	61	10
3	**14**	650	40	100	50	9

[a] Nitrogen carrier gas 19 ml / minute; [b] 1.77 Mmoles; [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.

Hydrogen atom of amino group in **3** is removed by calcium oxide to afford amide ion **17**. The amide ion **17** attacks benzene ring in two ways to give cyclic intermediates **18** and **19** which produce 4-substituted carbazole **6** and carbazole **4** by elimination of H^- and R^- ions. Cyclization position of the benzene ring by amide ion of **17** would depend on steric hindrance at the attack step, positive charge of the carbon atom in benzene ring and ability of R as a leaving group in the rearomatization step. When R is an amino group cyclization occurred mainly at the carbon atom in the benzene ring which has a hydrogen atom. In contrast, when R is a methoxyl group, cyclization occurred mainly at the carbon atom possesing the methoxyl group. In the case of R=NO_2, cyclization occurred exclusively at the carbon atom bearing the nitro group. The result shows that the nitro group induces a positive charge on the carbon atom in benzene and that it is a good leaving group.

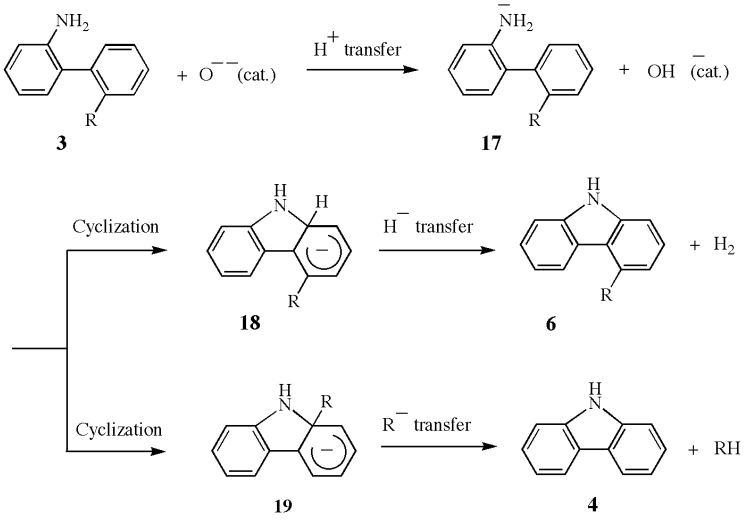
In the case of 2-amino-2'-methoxybiphenyl **3d**, dibenzofuran **9**, phenanthridine **8** were obtained along with carbazole **4** and 4-hydroxycarbazole **6e**. Plausible mechanisms are shown in Scheme 5.

Carbazole **4** and 4-hydroxycarbazole **6e** would be produced *via* **17d** as usual. Formation of dibenzofuran **9** is explained by initial demethylation of **3d** to **20** followed by cyclization to **21** and elimination of amide ion or from compound **22** by the similar mechanism. Phenanthridine **8** would be formed through methyl-transfer of **3d** to **22** and cyclization of anion **23**. In a separate experiment, 2-methylaminobiphenyl afforded *N*-methylcarbazole (14%), carbazole (24%) and phenanthridine (44%). The result supports the mechanism.

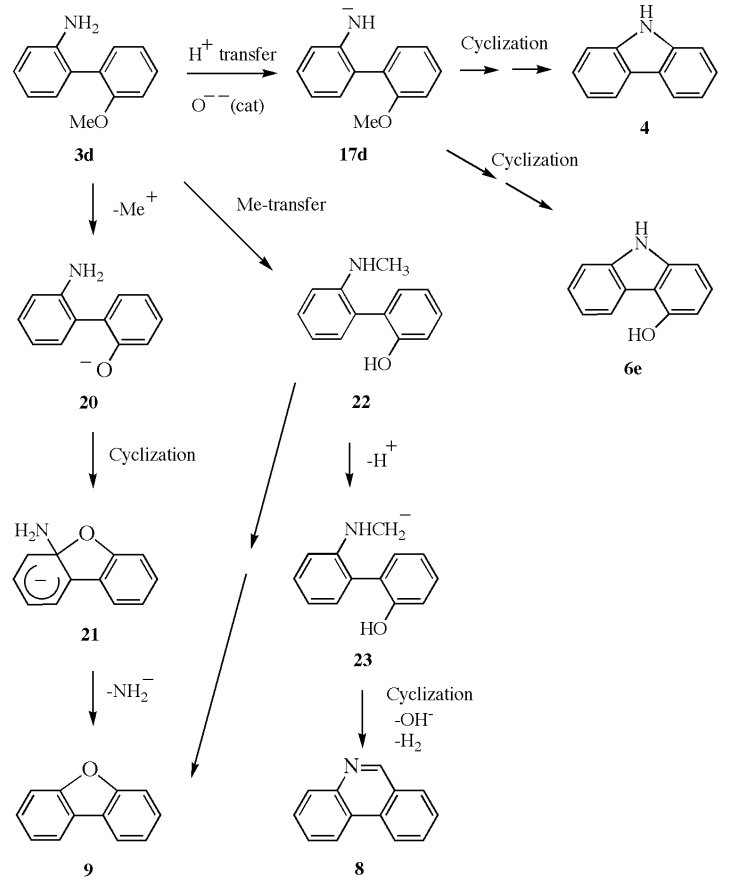
EXPERIMENTAL

The melting points are uncorrected. Column chromatography was performed on silica gel (Wakogel C-200). Unless otherwise

Scheme 4



Scheme 5



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 spectrometer. The ^{1}H and ^{13}C nmr spectra were determined at 500 MHz and 125 MHz on a Varian Unity plus-500W NMR spectrometer, using tetramethylsilane as the internal standard.

General Procedure for Intramolecular Cyclization Reaction of Aromatic Amines.

Elemental analysis apparatus (Micro Elemental Analyzer, Mitamura Riken Kogyo Inc.) was used for cyclization reaction. Granules of calcium oxide were obtained by grinding large pieces

of calcium oxide (Nakalai Tesque, Inc.) and collecting particles that passed through the 5 mm sieve and were retained by the 2 mm sieve. A quartz tube (66 cm in length, 12 mm i.d.) was packed to a height of 28 cm with the calcium oxide granules (18.0 g). The tube was positioned in 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 (450-650 °C). Starting material (1.77 mmoles) 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 500 °C, the stationary furnace was kept at 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. In the case of reaction temperature of 650 °C, the travelling furnace was kept at 650 °C. The travelling furnace moved gradually and reached to 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 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. The structure of products were determined from their spectra. Compounds **4**, **7**, **8**, **9**, **10**, **11**, **12**, **16** were identified by comparison of the ir, ^{1}H nmr and ^{13}C nmr spectra with those of comercially available samples. The ir , ^{1}H nmr and ^{13}C nmr spectra of compound **15** were identical with that of an authentic sample [9].

4-Aminocarbazole (**6b**).

Compound **6b** was obtained as colorless crystals, mp 188-192 °C from ethanol (lit. [21] mp 188-192 °C); ir (potassium bromide): 3410 (NH_2), 3340 (NH_2), 3190 cm^{-1} (NH); ^{1}H nmr (deuterioacetone): δ 5.10 (broad s, 2H, NH_2), 6.49 (d, J=8.0 Hz, 1H, Ar-H), 6.80 (d, J=8.0 Hz, 1H, Ar-H), 7.10 (dd, J=8.0 and 8.0 Hz, 1H, Ar-H), 7.12 (dd, J=8.0 and 8.0 Hz, 1H, Ar-H), 7.28 (dd, J=8.0 and 8.0 Hz, 1H, Ar-H), 7.43 (d, J=8.0 Hz, 1H, Ar-H), 8.13 (d, J=8 Hz, 1H, Ar-H), 10.24 (broad s, 1H, NH); ^{13}C nmr (deuterioacetone): δ 101.1 (d), 106.2 (d), 111.3 (d), 111.4 (s), 119.8 (d), 122.3 (d), 124.4 (s), 125.0 (d), 127.9 (d), 140.8 (s), 142.9 (s), 145.4 (s).

Anal. Calcd. for $C_{12}H_{10}N_2$: C,79.10; H,5.53; N,15.37. Found: C, 79.06; H, 5.64; N, 15.26.

4-Hydroxycarbazole (**6e**).

Compound **6e** was obtained as colorless crystals, mp 169-170 °C from ethanol (lit. [22] mp 169-170 °C); ir (potassium bromide): 3430 (NH), 3300 cm-1 (OH);); ^{1}H nmr (deuteriochloroform): δ 5.47 (broad s, 1H, OH), 6.58 (d, J=8.0 Hz, 1H, Ar-H), 7.01 (d, J=8.0 Hz, 1H, Ar-H), 7.22-7.27 (m, 2H, Ar-H_2), 7.39-7.41 (m, 2H, Ar-H_2), 8.06 (broad s, 1H, NH), 8.27 (d, J=8.0 Hz, 1H, Ar-H); ^{13}C nmr (deuteriochloroform): δ 103.3 (d), 105.1 (d), 110.0 (d), 111.8 (s), 119.7 (d), 122.3 (s), 122.7 (d), 125.1 (d), 126.5 (d), 138.8 (s), 141.4 (s), 151.9 (s).

Anal. Calcd. for $C_{12}H_9NO$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.56; H, 5.03; N, 7.69.

2-Hydroxydiphenylamine (**13**).

Compound **13** was obtained as colorless crystals, mp 67-68 °C from ethanol (lit. [23] mp 69-70 °C); ir (potassium bromide): 3360 cm^{-1} (NH and OH); ^{1}H nmr (deuteriochloroform): δ 5.28 (broad s, 1H, OH or NH), 5.85 (broad s, 1H, NH or OH), 6.77 (d, J=8.0 Hz, 2H, Ar-H_2), 6.87 (dd, J=8.0 and 8.0 Hz, Ar-H), 6.88 (dd, J=8.0 and 8.0 Hz, 1H, Ar-H), 6.97 (d, J=8.0 Hz, 1H, Ar-H), 7.07 (dd, J=8.0 and 8.0 Hz, 1H, Ar-H), 7.17 (d, J=8.0 Hz, 1H, Ar-H), 7.21 (dd, J=8.0 and 8.0 Hz, 2H, Ar-H_2); ^{13}C nmr (deuteriochloroform): δ 115.3 (d), 115.8 (d), 120.2 (d), 120.9 (d), 124.5 (d), 126.0 (d), 129.1 (s), 129.4 (d), 145.3 (s), 150.9 (s).

Anal. Calcd. for $C_{12}H_{11}NO$: C, 77.82; H, 5.99; N, 7.56. Found: C, 77.64; H, 6.08; N, 7.65.

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