

1-Arylpyrrole로부터 9-Arylcarbazole의 합성

鄭大一* · 金倫瑛 · 李龍均 · 朴유미 · 金寅植[†] · 成大東 · 金東賢[‡]

동아대학교 화학과

[†] 동아대학교 부속병원

[‡] 한국전력공사 에너지·환경고등연구소

(1996. 8. 14 접수)

Synthesis of 9-arylcarbazoles from 1-arylpyrroles

Dai-Il Jung*, Yun-Young Kim, Yong-Gyun Lee, You-Mi Park,

In-Shik Kim[†], Dae-Dong Sung, and Dong-Hyun Kim[‡]

Department of Chemistry, Dong-A University, Pusan 604-714, Korea

[†]Dong-A University Hospital, Pusan 604-714, Korea

[‡]Korea Electric Power Research Institute, Taejon 103-16, Korea

(Received August 14, 1996)

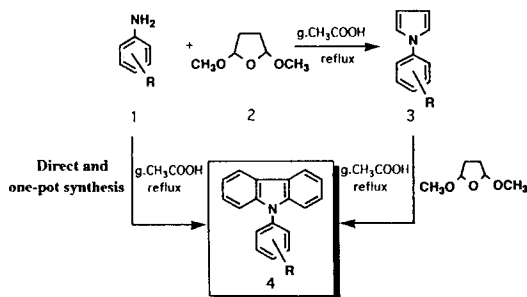
Carbazoles were discovered in anthracene oil of coal tar, and are the parent structure of a number of heterocyclic compounds. Much attention has been paid to carbazole derivatives recently as the materials for semiconductors¹ and photoconductive compounds.² Many conventional methods for synthesis of carbazoles were known such as Grabe-Ullmann methods³ and the Tauber methods.⁴

In the course of the investigation for the synthesis of pyrrole derivatives 3,⁵⁻⁷ we have found the formation of 9-arylcarbazoles 4 under refluxing glacial acetic acid. Thus we report the results here.

1-Arylpyrroles were prepared by the previously

published procedure.

Generally, synthetic methods of 1-arylpyrroles 3 from amines 1 and 2 have been known for a long time.⁸⁻¹⁰ 1-Arylpyrroles 3 were obtained in quantitative yields by the general method (Table 1). The effect of organic dicarboxylic acids on the synthesis of 3 was investigated (Table 2). Among organic dicarboxylic acids, adipic acid gave the highest yield of 3i (see Table 2, Entry 1). The yield of 3i was the lowest when acetonedicarboxylic acid



Scheme 1. Synthesis of 9-arylcarbazoles.

Table 1. Physical data of 1-arylpyrroles 3

	R	Yield(%) ^a	mp (°C)	lit. ⁸ mp(°C)
a	<i>p</i> -OCH ₃	98	108~109	108
b	<i>p</i> -CH ₃	97	78~79	
c	<i>p</i> -NO ₂	88	180~181 ⁷	180~181
d	<i>p</i> -F	96	56~60 ⁶	
e	<i>p</i> -Cl	96	42~43 ⁶	
f	<i>p</i> -Br	95	94~95 ^{6,7}	94~95
g	3,5-diCl	94	61~62 ⁶	
h	2,6-diCl	94	79~80 ⁶	
i	H	98	58~59 ^{6,7}	58~59
j	<i>m</i> -NO ₂	87	81~82 ⁷	81~82
k	<i>m</i> -Br	93	64~65 ^{6,7}	

^aIsolated yield.

Table 2. The yields of 1-phenylpyrrole **3i** depending on the dicarboxylic acids

Entry	Organic dicarboxylic acid	Reflux (min)	Yield(%) ^a 3i
1	Adipic acid	75	87
2	Tartaric acid	60	22
3	Acetonedicarboxylic acid	40	2(48) ^b
4	3-(carboxymethylthio) propionic acid	240	42
5	2-ketoglutaric acid	30	8
6	Bis(carboxymethyl) trithiocarbonate	30	23
7	Trans-3-hexenedionic acid	720	46

^aIsolated yield. ^bN-Phenylnortropinone.¹¹Table 3. Physical data of 9-arylcarbazoles **4**

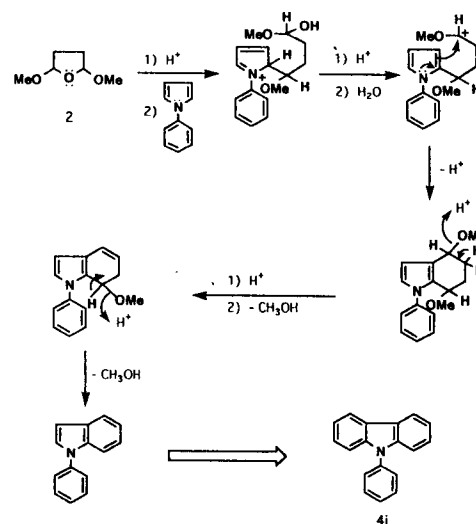
	Pyrrole	Reflux(h)	Yield(%) ^a	mp (°C)
a	<i>p</i> -OCH ₃	15	54	149~150
b	<i>p</i> -CH ₃	4	34	^b
c	<i>p</i> -NO ₂	28	30	^b
d	<i>p</i> -F	12	22	130~131
e	<i>p</i> -Cl	16	30	157~158
f	<i>p</i> -Br	18	40	159
g	3,5-diCl	9	23	^b
h	2,6-diCl	11	26	48~50
i	H	19	55	94~96
j	<i>m</i> -NO ₂	29	24	119~121
k	<i>m</i> -Br	18	23	^b

^aIsolated yield. ^bLiquid.

was used (Table 2, Entry 3), but *N*-phenylnortropinone was formed as the major product in 48% yield.

9-Arylcarbazoles **4** were formed by treatment of 1-arylpyrroles **3** with **2** in glacial acetic acid. The yields of **4**'s were summarized depending on the substituent(R) in Table 3.

A representative example of synthesis **4** is as the follow. The mixture of **3i** (5 mmol) and **2** (10 mmol) was refluxed in glacial acetic acid under N₂ gas for 19 h to afford **4i** in a 55% yield. Identification of 9-phenylcarbazole by ¹H NMR spectrum (CDCl₃, Me₄Si) showed 13 proton peaks corresponding to carbazoyl group and phenyl group at δ 7.25~8.18. Mass spectrum showed molecular ion peaks at *m/e* 243 (100%).



Scheme 2. Proposed mechanism for the formation of 9-phenylcarbazole.

Table 4. One-pot synthesis of 9-aryl carbazoles **4**

	R	Reflux(h)	Yield(%) ^a
a	<i>p</i> -OCH ₃	12	30
c	<i>p</i> -NO ₂	20	23
i	H	10	47
j	<i>m</i> -NO ₂	32	20
k	<i>m</i> -Br	18	15

^aIsolated yield. ^bLiquid.

But the synthesis of 9-alkylcarbazoles from the corresponding 1-alkylpyrroles was not successful.

In order to investigate the mechanism, the products in the reaction mixture were monitored with time by gas chromatography. 1-Arylindoles were detected by gas chromatography, which were confirmed with the authentic samples.

A possible mechanism for the formation of **4** may involve the cleavage reaction of furan ring by glacial acetic acid and subsequent formation of intermediates X and Y (Scheme 2).

9-arylcarbazoles **4** can also be prepared by one-pot reactions of the aromatic amines **1** and **2** in glacial acetic acid under N₂ gas. The results are listed in Table 4. However, the yields from the one-pot reaction are much lower than the reaction from 1-arylpyrroles.

EXPERIMENTAL SECTION

Melting points were determined on a Büchi 510 capillary melting point apparatus and uncorrected. Infrared spectra were recorded on a Perkin-Elmer 683 spectro-photometer. NMR spectra were recorded on a Varian XL-300 or Brüker AC 200 FT-NMR spectrometer in CDCl_3 containing Me_4Si as an internal reference. Mass spectra were obtained by using JEOL JMS DX 303 or HP 5892 Mass Spectrometer.

A typical procedure for the preparation of 9-phenylcarbazole 4i in glacial acetic acid. A mixture of **3i** (0.72 g, 5 mmol) and **2** (1.32 g, 10 mmol) in glacial acetic acid was refluxed for 19 h. Removal of the solvent under reduced pressure followed by flash column chromatography on a silica-gel (*n*-hexane : ethyl acetate = 10 : 1, v/v) gave the desired 9-phenylcarbazole **4i** as a solid (0.67 g, 55%); mp 94~96 °C; IR (KBr) 3050 (aromatic C-H) 1590, 1240, 760 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 7.25~8.18 (m, 13H, phenyl and carbazolyl group); ^{13}C NMR (CDCl_3 , 50.32 MHz) δ 129.9, 127.5, 125.9, 120.3, 119.9 109.8; Mass (m/e) 243(M^+), 166, 140, 77.

A typical procedure for the preparation of 9-(4'-methoxyphenyl) carbazole 4a by direct and one-pot reaction in glacial acetic acid. A mixture of **1a** (1.85 g, 15 mmol) and **2** (6.20 g, 45 mmol) in glacial acetic acid was refluxed for 12 h. The solvent was removed under aspirator pressure and the remaining sticky oil was separated by flash column chromatography on a silica gel (*n*-hexane). Yield 1.23 g (30%); IR (KBr) 3070 (aromatic C-H) 2950, 1600, 1210, 1120, 800 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 3.66 (s, 3H, CH_3) 7.25~8.18 (m, 12H, phenyl and carbazolyl group); Mass (m/e) 273(M^+), 258, 242, 166.

Physical data of 1-arylpyrroles. **1a** ^1H NMR (CDCl_3 , 200 MHz) δ 3.83 (s, 3H, CH_3), 6.32 (t, 2H), 6.92~6.99 (m, 4H), 7.28~7.33 (m, 2H); Mass (m/e) 173(M^+). **1b** ^1H NMR (CDCl_3 , 200 MHz) 2.34~2.46 (t, 3H, CH_3), 6.41~6.44 (t, 2H), 7.16~7.18 (t, 2H), 7.49~7.54 (m, 2H), 8.28~8.33 (m, 2H); Mass (m/e) 157(M^+). **1c** ^1H NMR (CDCl_3 , 200 MHz) δ 6.41~6.44 (t, 2H), 7.16~7.18 (t, 2H), 7.49~7.54 (m, 2H), 8.28~8.33 (m, 2H). **1g** IR (KBr) 3080s, 3120s (aro-

matic C-H), 1570s, 1590s (aromatic C=C) cm^{-1} ; ^1H NMR (CDCl_3 , 60 MHz) δ 6.35~6.41 (m, 2H, pyrrole C_3H , C_4H), 6.98~7.10 (m, 2H, pyrrole C_2H , C_5H), 7.15~7.41 (m, 3H, phenyl group); UV(EtOH) λ_{max} 262.2 nm. **1h** IR (KBr) 3080s, 3120s (aromatic C-H), 1560s (aromatic C=C) cm^{-1} ; ^1H NMR (CDCl_3 , 60 MHz) δ 6.35~6.51 (m, 2H, pyrrole C_3H , C_4H), 6.72~6.88 (m, 2H, pyrrole C_2H , C_5H), 7.26~7.65 (m, 3H, phenyl group); UV(EtOH) λ_{max} 240 nm. **1i** ^1H NMR (CDCl_3 , 200 MHz) δ 6.33~6.35 (t, 2H), 7.08~7.10 (t, 2H), 7.23~7.24 (m, 1H), 7.39~7.42 (m, 4H); Mass (m/e) 143(M^+). **1j** Mass (m/e) 188(M^+). **1k** Mass (m/e) 222(M^+).

Physical data of 9-arylcabazoles. **4a** IR (KBr) 3070~2980w (aromatic C-H), 2950~2800w (aliphatic C-H), 1600~1400s (aromatic C=C), 1120s (C-O), 1210s (C-N), 800~650w (=CH, aromatic OOP) cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 3.83 (s, 3H, CH_3), 7.02~8.19 (m, 12H, phenyl and carbazolyl group); Mass (m/e): 274 ($\text{M}^+ + 1$, 25), 273 (M^+ , 100), 258, 242, 166. **4b** IR (neat) 3060~2980w (aromatic C-H), 2950~2800w (aliphatic C-H), 1590 s (aromatic C=C), 1240s (C-N), 800~650w (=CH, aromatic OOP) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 2.34~2.46 (t, 3H, CH_3), 6.31~7.67 (m, 12H, phenyl and carbazolyl group); Mass (m/e): 257(M^+), 242, 242, 166. **4c** IR (neat) 3050~2900w (aromatic C-H), 1550s, 1390s (NO_2), 1500~1450s (aromatic C=C), 1230s (C-N), 760~720w (=CH, aromatic OOP) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 6.34~7.68 (m, 12H, phenyl and carbazolyl group); Mass (m/e) 288(M^+), 242, 166, 140, 46, 30. **4d** IR (neat) 3050~2900w (aromatic C-H), 1500~1450s (aromatic C=C), 1300s (aryl-F), 1210s (C-N), 760~720w (=CH, aromatic OOP) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 6.34~7.68 (m, 12H, phenyl and carbazolyl group); Mass (m/e), 262 ($\text{M}^+ + 1$, 18), 261 (M^+ , 100), 242, 166, 140, 75. **4e** IR (KBr) 3050~2950w (aromatic C-H), 1500~1450s (aromatic C=C), 1230s (C-N), 1120s (aryl-Cl), 760~710w (=CH, aromatic OOP) cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 7.26~8.16 (m, 12H, phenyl and carbazolyl group); Mass (m/e) 279 ($\text{M}^+ + 2$, 36), 277 (M^+ , 100), 242, 166, 140, 76. **14f** IR (KBr) 3030~3010w (aromatic C-H), 1500~1450s (aromatic C=C),

1230s (C-N), 1010s (aryl-Br), 760~710s (=CH, aromatic OOP) cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 7.25~8.19 (m, 12H, phenyl and carbazolyl group); ^{13}C NMR (CDCl_3 , 50.32 MHz) δ 133.13, 128.75, 126.10, 123.52, 120.41, 120.24, 109.57; Mass (m/e) 323 ($M^+ + 2$, 108), 321 (M^+ , 100), 241, 166, 140, 76. **4g** IR (neat) 3100~3000w (aromatic C-H), 1580~1550s (aromatic C=C), 1220s (C-N), 1130s (aryl-Cl), 750~740s (=CH, aromatic OOP) cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 6.68~8.26 (m, 11H, phenyl and carbazolyl group); Mass (m/e): 315 ($M^+ + 4$, 10), 313 ($M^+ + 2$, 69), 311 (M^+ , 100), 276, 242, 166, 75, 62. **4h** IR (KBr) 3150~3000w (aromatic C-H), 1570~1550s (aromatic C=C), 1220s (C-N), 1130m (aryl-Cl), 750~740s (=CH, aromatic OOP) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 6.73~7.71 (m, 11H, phenyl and carbazolyl group); Mass (m/e) 315 ($M^+ + 4$, 10), 313 ($M^+ + 2$, 60), 311 (M^+ , 100), 276, 242, 166, 75, 62. **4i** IR (KBr) 3050~2950w (aromatic C-H), 1590s (aromatic C=C), 1240s (C-N), 760~700s (=CH aromatic OOP) cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 7.25~8.18 (m, 13H, phenyl and carbazolyl group); ^{13}C NMR (CDCl_3 , 50.32 MHz) δ 129.89, 127.45, 125.91, 120.30, 119.89, 109.76; Mass (m/e): 244 ($M^+ + 1$, 23), 243 (M^+ , 100), 166, 140, 77. **4j** IR (neat) 3050~2900w (aromatic C-H), 1550s, 1390s (NO_2), 1500~1450s (aromatic C=C), 1230s (C-N), 760~720w (=CH, aromatic OOP) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 6.34~7.68 (m, 12H, phenyl and carbazolyl group); Mass (m/e): 288, 242, 166, 140, 46, 30. **4k** IR (neat) 3030~3010w (aromatic C-H), 1500~1450s (aromatic C=C), 1215s (C-N), 1005s (aryl-Br), 770~710s (=CH, aromatic OOP) cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 7.25~8.20 (m, 12H, phenyl and carbazolyl group); Mass (m/e): 323 ($M^+ + 2$, 103), 321 (M^+ , 100), 241, 166, 140, 76.

Acknowledgement. The authors are grateful for the financial support from Basic Science Research Institute and Dong-A University.

REFERENCE

1. (a) Block, H.; Cowd, M. A.; Walker, S. M. *Polymer* **1977**, *18*, 781. (b) Hermann, A. M.; Rembaum, A. *J. Polym. Sci., Polym. Symp.* **1967**, *17*, 107. (c) Kanega, H. H.; Shiota, Y.; Mikawa, H. *J. Chem. Soc., Chem. Commun.* **1984**, 158. (d) Murray, R. W. *Annu. Rev. Mater. Sci.* **1984**, *14*, 145.
2. (a) Hisch, R.; Pohl, R. W. *Z. Phys.* **1933**, *87*, 78. (b) Hogel, H. *J. Phys. Chem.* **1965**, *69*, 755. (c) Lardon, M.; Dorller, E. L.; Weigl, J. W. *Mol. Crystallot.* **1967**, *2*, 241. (d) Gill, W. D. *J. Appl. Phys.* **1972**, *43*, 5033. (e) Schaffert, R. M. *IBM J. Res. Dev.* **1971**, *15*, 75.
3. (a) Graeke, O. H.; Ullmann, F. *Ann.* **1896**, 291, 16. (b) Graeke, O. H.; Ullmann, F. *Ann.* **1947**, 937.
4. Tauber, E. *Ber.* **1891**, *24*, 200.
5. Kashima, C.; Hibi, S.; Marugama, T.; Omote, Y. *Tetrahedron Lett.* **1986**, *27*, 2131.
6. Jung, D. I.; Kim, Y. Y.; Yoo, B. G.; Lee, Y. G.; Choi, S. K. *J. Korean Chem. Soc.* **1993**, *37*, 982.
7. Jung, D. I.; Kim, Y. Y.; Yoo, B. G.; Lee, Y. G.; Choi, S. K. *Bull. Korean Chem. Soc.* **1994**, *15*, 168.
8. Elming, N.; Clauson-Kass, N. *Acta. Chem. Scand.* **1952**, *6*, 867.
9. Chiang, Y.; Hinman, R. L.; Teodoropulos, S.; Wipple, E. B. *Tetrahedron* **1967**, *23*, 745.
10. Josey, A. D. *Org. Syn. Coll.* **1973**; Vol. V, pp 716.
11. Candy, C. F.; Jones, R. A.; Wright, P. H. *J. Chem. Soc.* **1970**, 2563.
12. *N*-Phenylnortropinone. ^1H NMR (CDCl_3 , 200 MHz) δ 4.32 (s, 2H), 2.45~2.34 (dd, 2H), 2.03~1.82 (m, 4H), 1.49~1.42 (m, 2H), 7.35~6.75 (m, aromatic 5H); Mass (m/e) 201(M^+), 143, 104, 77, 51.