Journal of the Korean Chemical Society
1996, *Vol. 40, No. 11*
Printed in the Republic of Korea

단 신

1-Arylpyrrole로부터 9-Arylcarbazole의 합성

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(1996. 8. 14 접수)

Synthesis of 9-arylcarbazoles from 1-arylpyrroles

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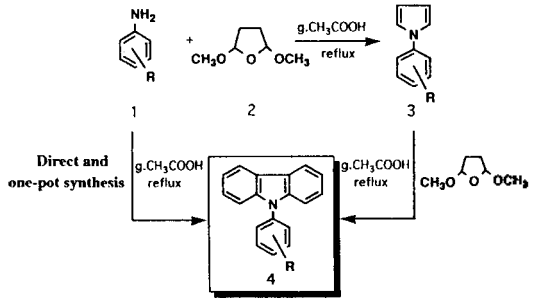
(Received August 14, 1996)

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 semiconductors[1] and photoconductive compounds.[2] Many conventional methods for synthesis of carbazoles were known such as Grabe-Ullmann methods[3] 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.



Scheme 1. Synthesis of 9-arylcarbazoles.

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

Table 1. Physical data of 1-arylpyrroles **3**

	R	Yield(%)[a]	mp (℃)	lit.[8] mp(℃)
a	*p*-OCH_3	98	108~109	108
b	*p*-CH_3	97	78~79	
c	*p*-NO_2	88	180~181[7]	180~181
d	*p*-F	96	56~60[6]	
e	*p*-Cl	96	42~43[6]	
f	*p*-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	*m*-NO_2	87	81~82[7]	81~82
k	*m*-Br	93	64~65[6,7]	

[a]Isolated 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

[a]Isolated yield. [b]*N*-Phenylnortropinone.[11]

Table 3. Physical data of 9-arylcarbazoles **4**

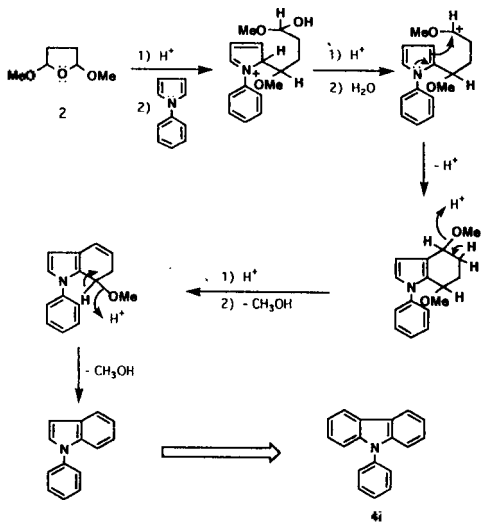
	Pyrrole	Reflux(h)	Yield(%)[a]	mp (℃)
a	*p*-OCH_3	15	54	149~150
b	*p*-CH_3	4	34	[b]
c	*p*-NO_2	28	30	[b]
d	*p*-F	12	22	130~131
e	*p*-Cl	16	30	157~158
f	*p*-Br	18	40	159
g	3,5-diCl	9	23	[b]
h	2,6-diCl	11	26	48~50
i	H	19	55	94~96
j	*m*-NO_2	29	24	119~121
k	*m*-Br	18	23	[b]

[a]Isolated yield. [b]Liquid.

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 summerized 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 N_2 gas for 19 h to afford **4i** in a 55% yield. Identification of 9-phenylcarbazole by ^1H NMR spectrum ($CDCl_3$, Me_4Si) showed **13** proton peaks corresponding to carbazolyl 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	*p*-OCH_3	12	30
c	*p*-NO_2	20	23
i	H	10	47
j	*m*-NO_2	32	20
k	*m*-Br	18	15

[a]Isolated yield. [b]Liquid.

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 comfirmed 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 N_2 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 $^{-1}$; ^{1}H 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 $^{-1}$; ^{1}H 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 ^{1}H 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** ^{1}H 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** ^{1}H 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 (aromatic C-H), 1570s, 1590s (aromatic C=C) cm $^{-1}$; ^{1}H 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 $^{-1}$; ^{1}H 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** ^{1}H 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-arylcarbazoles. 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 $^{-1}$; ^{1}H 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 (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 $^{-1}$; ^{1}H 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 $^{-1}$; ^{1}H 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 $^{-1}$; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.34~7.68 (m, 12H, phenyl and carbazolyl group); Mass (m/e), 262 (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 $^{-1}$; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.26~8.16 (m, 12H, phenyl and carbazolyl group); Mass (m/e) 279 (M^++2, 36), 277 (M^+, 100), 242, 166, 140, 76. **4f** IR (KBr) 3030~3010w (aromatic C-H), 1500~1450s (aromatic C=C),

1230s (C-N), 1010s (aryl-Br), 760~710s (=CH, aromatic OOP) cm $^{-1}$; ^{1}H 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 $^{-1}$; ^{1}H 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. **14h** IR (KBr) 3150~3000w (aromatic C-H), 1570~1550s (aromatic C=C), 1220s (C-N), 1130m (aryl-Cl), 750~740s (=CH, aromatic OOP) cm $^{-1}$; ^{1}H 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 $^{-1}$; ^{1}H 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 $^{-1}$; ^{1}H 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 $^{-1}$; ^{1}H 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.

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12. *N*-Phenylnortropinone, ^{1}H 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.