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Registry No. **1a**, 22430-47-3; **1b**, 133683-82-6; **4**, 110187-19-4; **5**, 104226-70-2; **6**, 114730-22-2; **7** (isomer 1), 135570-10-4; **7** (isomer 2), 135570-11-5; **8** (isomer 1), 135570-12-6; **8** (isomer 2), 135570-13-7; **9** (isomer 1), 135570-16-0; **9** (isomer 2), 135570-17-1; **10** (isomer 1), 135570-14-8; **10** (isomer 2), 135570-15-9; **11** (isomer 1), 135637-50-2; **11** (isomer 2), 135637-51-3; $H_3C(CH_2)COCl$, 334-19-0; $ClCO(CH_2)_5COCl$, 142-79-0; $H_3C(CH_2)_7COCl$, 764-85-2; $MeO_2CCH_2CH_2COCl$, 1490-25-1; $MeO_2C(CH_2)COCl$, 1501-26-4.

Organic Reactions Catalyzed by Solid Superacids. 10.[1] Perfluorinated Sulfonic Acid Resin (Nafion-H) Catalyzed Ring Closure Reaction of 2,2′-Diaminobiphenyls. A Preparative Route to Carbazoles

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Introduction

The acid-catalyzed ring closure of 2,2′-diaminobiphenyls to corresponding carbazoles has been studied using various acids.[2-4] However, these methods require elevated temperatures (>200 °C), long reaction times, and excess of protic acids. Furthermore, some of these reactions were plagued with undesirable side products during cyclization.[4] Therefore, the scope and selectivity for the preparation of carbazole derivatives have been limited.

Recently, we have found that Nafion-H, a perfluorinated sulfonic acid resin, catalyzes ring closure of 2,2′-dihydroxybiphenyls to dibenzofuran derivatives under relatively mild conditions.[5]

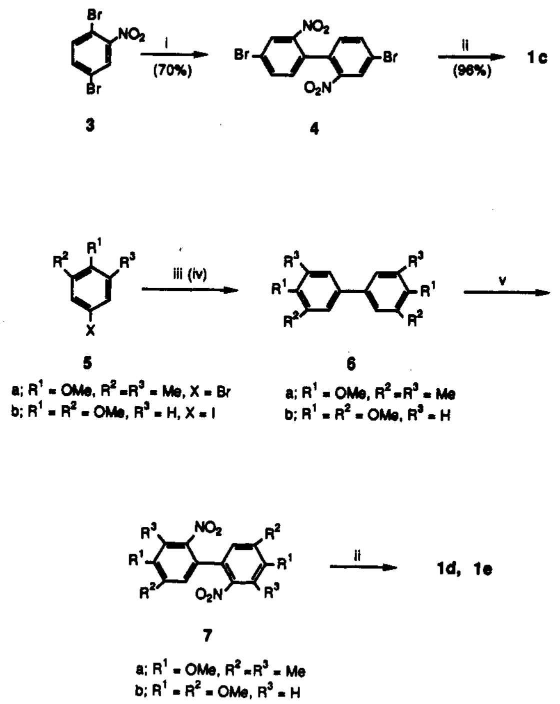
Now we wish to report an efficient and mild procedure for the ring closure of 2,2′-diaminobiphenyls in the presence of the solid superacid, Nafion-H, to afford carbazole derivatives in good to moderate yields.

Results and Discussion

The preparative route for 2,2′-diamino-4,4′-dibromobiphenyl (**1c**), 2,2′-diamino-3,3′,5,5′-tetramethyl-4,4′-dimethoxybiphenyl (**1d**), and 2,2′-diamino-4,4′,5,5′-tetramethoxybiphenyl (**1e**) is shown in Scheme I, and the preparation of other diaminobiaryls **1a** and **1b** was carried out by the reduction of the corresponding dinitrobiaryls with Sn–HCl in ethanol according to the literature.[6-8]

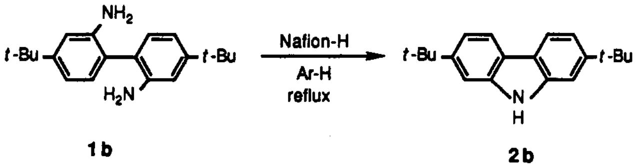
The attempted ring closure reaction of 4,4′-di-*tert*-butyl-2,2′-diaminobiphenyl (**1b**), performed in refluxing *o*-xylene for 36 h in the presence of Nafion-H, failed. Only starting material was recovered. However, when the reaction was carried out in refluxing 4-*tert*-butyltoluene, 4-*tert*-butyl-*o*-xylene, or nitrobenzene, the desired product, 2,7-di-*tert*-butylcarbazole (**2b**), was obtained (Table I). In the case of 4-*tert*-butyltoluene reflux, it takes more than 36 h to complete the reaction, but under 4-*tert*-butyl-*o*-xylene or nitrobenzene reflux only 12 h are required.

Scheme I[a]



[a] Key: (i) Cu/DMF, 120 °C for 1 h; (ii) Sn/HCl/EtOH; (iii) $NiCl_2$/Zn/triphenylphosphine/DMF, 50–60 °C for 12 h; (iv) Cu, 260 °C for 3 h; (v) fuming HNO_3/Ac_2O.

Table I. Nafion-H-Catalyzed Condensation of 4,4′-Di-*tert*-butyl-2,2′-diaminobiphenyls 1b



1b **2b**

run	solvent	amount of Nafion-H (wt %)	reaction time (h)	yields[a] (%) 1b	yields[a] (%) 2b
1	*o*-xylene	50	36	100	0
2	4-*tert*-butyltoluene	50	12	41	54
3	4-*tert*-butyltoluene	100	12	35	61
4	4-*tert*-butyltoluene	100	48	0	98 (88)[b]
5	4-*tert*-butyl-*o*-xylene	50	12	5	90
6	4-*tert*-butyl-*o*-xylene	50	12	4	90 (87)[b]
7	nitrobenzene	50	12	0	95 (93)[b]
8	biphenyl[c]	100	12	0	0[d]

[a] Yields are determined by GLC analyses. [b] Isolated yields are shown in parentheses. [c] Reaction temperature: 250–260 °C. [d] Carbazole **2a** was obtained in quantitative yield.

However, when nitrobenzene was used as a solvent, the highest isolated yield of **2b** (run 7) was obtained, but a remarkable deactivation of catalyst was observed because regeneration of catalyst could not be achieved to the original catalytic activity.

Product **2b** was isolated by simple filteration of the hot reaction mixture followed by distillation of the filtrate.

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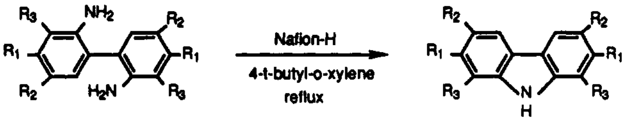
Table II. Nafion-H-Catalyzed Condensation of 2,2′-Diaminobiphenyls 1[a]



1

2

a ; R$_1$ = R$_2$ = R$_3$ = H
b ; R$_1$ = t-Bu ; R$_2$ = R$_3$ = H
c ; R$_1$ = Br ; R$_2$ = R$_3$ = H
d ; R$_1$ = OMe; R$_2$ = R$_3$ = Me
e ; R$_1$ = R$_2$ = OMe; R$_3$ = H

run	substrate 1	reaction time (h)	product yield[b] (%)
1	**1a**	12	**2a** (100), **1a** (0)
2	**1b**	12	**2b** (90), **1b** (5)
3	**1c**	12	**2c** (50), **1c** (50)
4	**1c**	24	**2c** (58), **1c** (37)
5	**1d**	12	**2d** (62), **1d** (17)
6	**1e**	12	**2e** (60), **1e** (26)

[a] Catalyst 50 wt %. [b] Yields were determined by GLC analyses.

The reaction was very clean. However, it is not clear whether ammonia, an expected byproduct of the reaction, might be removed by gas from the reaction mixture or react with the SO$_3$H group in Nafion-H to form Nafion-NH$_4^+$. The proportion of catalyst required, as a function of the amount of 2,2′-diaminobiphenyl **1b**, was between 30 and 50 wt %. Optimum yield of carbazole **2b** was obtained with 50 wt % of catalyst, whereas the use of 30 wt % of catalyst gave only slightly lower yield.

Previously, we have reported[4] that treatment of 4,4′-di-*tert*-butyl-2,2′-diaminobiphenyl (**1b**) with 85% phosphoric acid under refluxing conditions (220–250 °C) for 24–120 h underwent ring closure to give de-*tert*-butylated product carbazole **2a** in 20–40 % yield along with a large amount of unseparable resinous materials. However, in the present work, only ring closure reaction to afford **2b** was observed, but no concomitant de-*tert*-butylation took place under 4-*tert*-butyl-*o*-xylene.

We previously reported[9] a convenient method using toluene as an acceptor for the *tert*-butyl group in the Nafion-H-catalyzed de-*tert*-butylation of 2,7-di-*tert*-butylcarbazole (**2b**), affording the desired carbazole **2a**. Utilizing this reaction, we have developed a one-pot procedure to convert 4,4′-di-*tert*-butyl-2,2′-diaminobiphenyl (**1b**) directly to carbazole **2a** much more conveniently. Thus, heating of compound **1b** in biphenyl, a good acceptor for the *tert*-butyl group,[9] at 230–240 °C for 12 h with 100 wt % of Nafion-H results in complete removal of *tert*-butyl groups to give the desired carbazole **2a** in quantitative yield (Table I, run 8).

Nafion-H-catalyzed ring closure was further applied to not only 2,2′-diaminobiphenyl (**1a**) but also bromo-, methyl-, and methoxy-substituted 2,2′-diaminobiphenyl (**1c**–**1e**) to afford carbazole **2a** and corresponding carbazole derivatives **2c**–**2e**. As shown in Table II, the present method provides good yields and easy isolation of the products, and no concomitant trans bromination and demethylation were observed under the reaction conditions.

Furthermore, ready regeneration of the catalyst without the loss of catalytic activity offers an advantage over previously reported methods.

Experimental Section

All melting and boiling points are uncorrected. NMR spectra were recorded at 270 MHz on a Nippon Denshi JEOL FT-270 NMR spectrometer with Me$_4$Si as an internal reference. IR spectra were measured as KBr pellets or as liquid films on NaCl plates on a Nippon Denshi JIR-AQ2OM spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-01SA-2 spectrometer at 75 eV using a direct inlet system.

Nafion-H catalyst was prepared from commercially available (Du Pont) Nafion-K resin, as previous described.[10]

Preparation of 4,4′-Dibromo-2,2′-dinitrobiphenyl (4). A mixture of 12 g (42.7 mmol) of 2,5-dibromonitrobenzene (**3**), 6 g of Cu powder (100 mesh), and 80 mL of DMF was heated at 120 °C with stirring for 2 h. After the reaction, the reaction mixture was cooled to room temperature and dissolved in benzene. Unreacted Cu powder and insoluble materials were filtered off, and the benzene solution was washed with water, dried over Na$_2$SO$_4$, and evaporated in vacuo. The residue was recrystallized from ethanol to give 6.0 g (70%) of **4**: pale yellow prisms (EtOH); mp 146–148 °C (lit.[11] mp 150 °C).

Preparation of 4,4′-Dibromo-2,2′-diaminobiphenyl (1c). To a solution of 4.02 g (10 mmol) of **4** and 20 mL of concentrated HCl in 50 mL of EtOH was gradually added 4.74 g of Sn powder. After the reaction mixture was refluxed for 30 min, it was poured into a large amount of ice–water, basified with 10% NaOH solution, and extracted with ether. The other solution was washed with water, dried over Na$_2$SO$_4$, and evaporated in vacuo. The residue was recrystallized from ethanol to give 3.0 g (95.5%) of **1c**: pale brown prisms (EtOH); mp 99–105 °C; IR (KBr) 3404, 3394, 3191, 1638, 1582, 1556, 1476, 1405, 851, 815, 793, 769, 740 cm^{-1}; NMR (CDCl$_3$) δ 3.74 (4 H, br s), 6.93 (6 H, br s); mass (*m*/*e*) 342, 344, 346 (M$^+$). Anal. Calcd for C$_{12}$H$_{10}$N$_2$Br$_2$: C, 42.14; H, 2.95; N, 8.19. Found: C, 42.16; H, 3.18; N, 8.23.

Preparation of 3,3′,4,4′-Tetramethyl-4,4′-dimethoxybiphenyl (6a). A mixture of 130 mg of NiCl$_2$, 2 g of triphenylphosphine, 2 g of zinc powder, and 10 mL of DMF was heated at 50–60 °C for 1 h while being stirred. To this reaction mixture was added 4.3 g (20 mmol) of **5a** in 5 mL of DMF.[12] After the reaction mixture was stirred at 50–60 °C for 12 h, it was poured into 200 mL of cold aqueous HCl and extracted with dichloromethane, and the dichloromethane extract was washed with water, dried over Na$_2$SO$_4$, and evaporated in vacuo. The residue was chromatographed on silica gel with benzene as an eluent to give 3.13 g (58%) of **6a**: colorless prisms (hexane); mp 99–100 °C (lit.[13] mp 99–99.5 °C).

Preparation of 2,2′-Dinitro-3,3′,5,5′-tetramethyl-4,4′-dimethoxybiphenyl (7a). To a solution of 5.4 g (10 mmol) of **6a** in 100 mL of Ac$_2$O was added at room temperature a solution of 6 mL of fuming HNO$_3$ (d = 1.5) and 10 mL of AcOH. The reaction mixture was stirred for 1 h, poured into a large amount of water, and extracted with dichloromethane, and the dichloromethane solution was washed with water, dried over Na$_2$SO$_4$, and evaporated in vacuo. The residue was recrystallized from ethanol to give 3.3 g (91.7%) of **7a**: pale brown prisms (EtOH); mp 168–173 °C; IR (KBr) 3030, 1529, 1467, 1396, 1381, 1360, 1271, 1224, 1053, 1000 cm^{-1}; NMR (CDCl$_3$) δ 2.28 (6 H, s), 2.30 (6 H, s), 3.77 (6 H, s), 6.96 (2 H, s); mass (*m*/*e*) 360 (M$^+$). Anal. Calcd for C$_{18}$H$_{20}$O$_6$N$_2$: C, 60.00; H, 5.59; N, 7.77. Found: C, 60.27; H, 5.63; N, 6.97.

Preparation of 2,2′-Diamino-3,3′,5,5′-tetramethyl-4,4′-dimethoxybiphenyl (1d). To a solution of 1.80 g (5 mmol) of **7a** and 15 mL of concentrated HCl in 40 mL of EtOH was gradually added 3.76 g of Sn powder. After the reaction mixture was refluxed for 30 min, it was poured into a large amount of ice-water, basified with 10% NaOH solution, and extracted with ether. The ether solution was washed with water, dried over Na$_2$SO$_4$, and evaporated in vacuo. The residue was recrystallized from hexane to give 950 mg (63.3%) of **1d**: pale yellow prisms (hexane); mp 154–156 °C; IR (KBr) 2939, 1615, 1471, 1429, 1279, 1140, 1119, 1009 cm^{-1}; NMR (CDCl$_3$) δ 2.15 (6 H, s), 2.21 (6 H, s), 3.52 (4 H, br s), 3.73 (6 H, s), 6.98 (2 H, s); mass (*m*/*e*) 300 (M$^+$). Anal. Calcd for C$_{18}$H$_{24}$O$_2$N$_2$: C, 71.97; H, 8.05; N, 9.33. Found: C, 72.44; H, 7.97; N, 9.17.

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Preparation of 3,3′,4,4′-Tetramethoxybiphenyl (6b). A mixture of 12 g (42.7 mmol) of 3,4-dimethoxyiodobenzene (**5b**) and 20 g of Cu powder (100 mesh) was heated at 260–280 °C with stirring for 2 h. After the reaction, the reaction mixture was cooled to room temperature and dissolved in benzene. Unreacted Cu powder and insoluble materials were filtered off, and the benzene solution was washed with water, dried over Na_2SO_4, and evaporated in vacuo. The residue was recrystallized from ethanol to give 11.6 g (87.4%) of **6b**: pale yellow prisms (EtOH); mp 124–126 °C; IR (KBr) 2931, 2833, 1574, 1501, 1463, 1450, 1441, 1418, 1405, 1250, 1229, 1208, 1176, 1166, 1144, 1139, 1024, 809, 764 cm^{-1}; NMR ($CDCl_3$) δ 3.92 (6 H, s), 3.95 (6 H, s), 6.93 (2 H, d, J = 7.81 Hz), 7.06 (2 H, d, J = 1.95 Hz), 7.11 (2 H, dd, J = 1.95, 7.81 Hz); mass (*m/e*) 274 (M^+). Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.01; H, 6.61. Found: C, 69.61; H, 6.68.

Preparation of 2,2′-Dinitro-4,4′,5,5′-tetramethoxybiphenyl (7b). To a solution of 822 mg (3 mmol) of **6b** in 15 mL of Ac_2O was added at room temperature a solution of 1 mL of fumine HNO_3 (d = 1.5) and 2 mL of AcOH. The reaction mixture was stirred for 10 min and poured into a large amount of water, extracted with dichloromethane, and the dichloromethane solution was washed with water, dried over Na_2SO_4, and evaporated in vacuo. The residue was recrystallized from ethanol to give 700 mg (64.2%) of **7b**: pale yellow prisms (hexane/benzene (1:1)); mp 210–212 °C; IR (KBr) 3030, 1571, 1516, 1329, 1292, 1270, 1211, 1065 cm^{-1}; NMR ($CDCl_3$) δ 3.93 (6 H, s), 4.02 (6 H, s), 6.64 (2 H, s), 6.98 (2 H, s); mass (*m/e*) 364 (M^+). Anal. Calcd for $C_{16}H_{16}O_8N_2$: C, 52.75; H, 4.43; N, 7.69. Found: C, 52.99; H, 4.47; N, 7.20.

Preparation of 2,2′-Diamino-4,4′,5,5′-tetramethoxybiphenyl (1e). To a solution of 1.0 g (10 mmol) of **7b** and 20 mL of concentrated HCl in 40 mL of EtOH was gradually added 2.37 g of Sn powder. After the reaction mixture was refluxed for 30 min, it was poured into a large amount of ice–water, basified with 10% NaOH solution, and extracted with ether. The ether solution was washed with water, dried over Na_2SO_4, and evaporated in vacuo. The residue was recrystallized from benzene to give 700 mg (83.7%) of **1e**: pale brown prisms (benzene); mp 175–176 °C; IR (KBr) 3340, 1527, 1511, 1463, 1452, 1440, 1260, 1210, 1167, 1154, 1141, 1039, 1033, 1002, 836 cm^{-1}; NMR ($CDCl_3$) δ 3.60 (4 H, broad s), 3.81 (6 H, s), 3.88 (6 H, s), 6.39 (2 H, s), 6.68 (2 H, s); mass (*m/e*) 304 (M^+). Anal. Calcd for $C_{16}H_{20}O_4N_2$: C, 63.14; H, 6.62; N, 9.20. Found: C, 63.30; H, 6.68; N, 8.89.

General Procedure for the Ring Closure of 2,2′-Diaminobiphenyl (1) in the Presence of Nafion-H. A mixture of 500 mg of **1** and 250 mg (50 wt %) of Nafion-H in 5 mL of 4-*tert*-butyltoluene, 4-*tert*-butyl-*o*-xylene, or nitrobenzene was refluxed until completion of the reaction as monitored by GLC analysis (silicon OV-1, 2 m). The solid sulfonic acid resin was filtered off and the filtrate analyzed by GLC. The filtrate was evaporated in vacuo. The residue was recrystallized.

Carbazole 1a: colorless prisms (EtOH); mp 244–245 °C (lit.[14] mp 245 °C).

2,7-Di-*tert*-butylcarbazole (1b): colorless plates (hexane); mp 155–156 °C (lit.[7] mp 155–156 °C).

2,7-Dibromocarbazole (2c): colorless prisms (hexane/benzene (1:1)); mp 198–203 °C; IR (KBr) 3399, 3030, 1599, 1442, 1421, 1325, 1052, 857, 805 cm^{-1}; NMR ($CDCl_3$) δ 7.35 (2 H, dd, J = 8.3 Hz, J = 1.5 Hz), 7.57 (2 H, d, J = 1.5 Hz), 7.88 (2 H, d, J = 8.3 Hz), 8.11 (1 H, s); mass (*m/e*) 323, 325, 327 (M^+). Anal. Calcd for $C_{12}H_7NBr_2$: C, 44.35; H, 2.17; N, 4.31. Found: C, 44.61; H, 2.49; N, 4.11.

1,3,6,8-Tetramethyl-2,7-dimethoxycarbazole (2d): pale yellow prisms (EtOH); mp 171–172 °C; IR (KBr) 3359, 3030, 2960, 2938, 2913, 2853, 1458, 1402, 1296, 1197, 1169, 1091, 1002, 993, 857 cm^{-1}; NMR ($CDCl_3$) δ 2.43 (6 H, s), 2.48 (6 H, s), 3.79 (6 H, s), 7.49 (1 H, br s), 7.60 (2 H, s); mass (*m/e*) 283 (M^+). Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47; N, 4.94. Found: C, 76.99; H, 7.55; N, 4.89.

2,3,6,7-Tetramethoxycarbazole (2e): pale yellow prisms (hexane/benzene (1:3)); mp 186–190 °C dec; IR (KBr) 3398, 3070, 2946, 2837, 1621, 1490, 1443, 1276, 1226, 1195, 1158, 1128, 781 cm^{-1}; NMR ($CDCl_3$) δ 3.95 (6 H, s), 4.00 (6 H, s), 6.91 (2 H, s), 7.40 (2 H, s), 7.72 (1 H, br s); mass (*m/e*) 287 (M^+). Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.87. Found: C, 67.10; H, 6.05; N, 4.78.

One-Pot Procedure for the Conversion of 4,4′-Di-*tert*-butyl-2,2′-diaminobiphenyl (1b) to 2a. A mixture of 592 mg (2 mmol) of **1b**, 592 mg (100 wt %) of Nafion-H, and 1.54 g (10 mmol) of biphenyl was heated at 250–260 °C for 12 h. After the reaction mixture was cooled to room temperature, it was dissolved with diethyl ether and the insoluble resin was removed by filtration. The solvent was evaporated from the filtrate. The residue was washed several times with hot hexane to give 250 mg (75%) of carbazole (**2a**) as colorless prisms.

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