# Studies on Selective Preparation of Aromatic Compounds; 21. A Convenient Preparation of Carbazole and 4-Methylcarbazole from Biphenyl Using *t*-Butyl Groups as a Positional Protective Group[1]

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It has been previously reported that the *t*-butyl group can be used as a positional protective group for the preparation of some phenolic compounds[2-6], diarylalkanes[7], 1,2-di- and 1,2,3-trisubstituted benzenes[8], 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene[9], dimethylmetacyclophane[10], aryl 4-hydroxyphenyl ethers[11], and 2-mono- and 2,2′-disubstituted biphenyls[1].

Although carbazole (**2a**)[12] and 4-methylcarbazole (**2b**)[12] have been prepared by the reductive cyclization of the corresponding 2-nitrobiphenyls **1** with triethyl phosphite, 2-nitrobiphenyl (**1a**) is only a minor product of the nitration of biphenyl (**3**) and the preparative routes to 2-nitro-2′-methylbiphenyl (**1b**) from easily available compounds seem to be too long for practical purposes.

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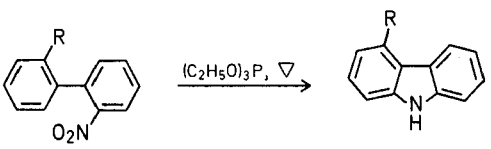


**1a** R = H
**b** R = $CH_3$

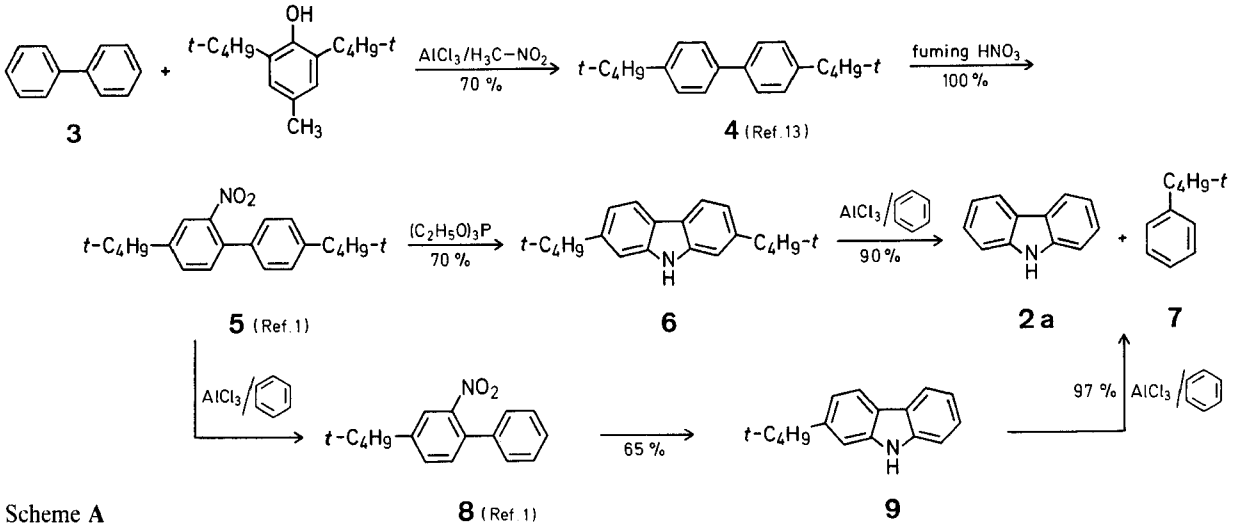
**2a, b**

We now wish to report a convenient preparation of **2a** and **2b** in four and six steps from **3**, respectively, involving use of the *t*-butyl group as a positional protective group (see Schemes **A** and **B**, respectively).

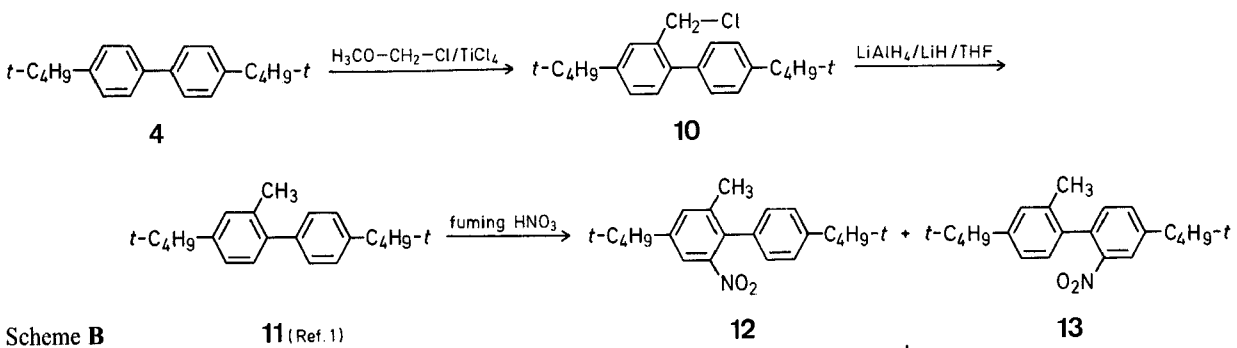
The aluminum chloride-catalyzed trans-*t*-butylation of **6**, **9**, and **14** in benzene afforded the desired **2a** and **2b** in good yields together with formation of *t*-butylbenzene (**7**), respectively.

**2,7-Di-*t*-butylcarbazole (6):**

After a mixture of 2-nitro-4,4'-di-*t*-butylbiphenyl[1] (**5**; 7.4 g, 25 mmol) and triethyl phosphite (16.5 g, 100 mmol) has been heated under reflux for 9 h under an atmosphere of nitrogen, it is distilled under reduced pressure to leave a residue which is column chromatographed on silica gel using hexane as an eluent to give **6** as colorless prisms; yield: 4.75 g (72 %); m.p. 155–156° (from hexane).



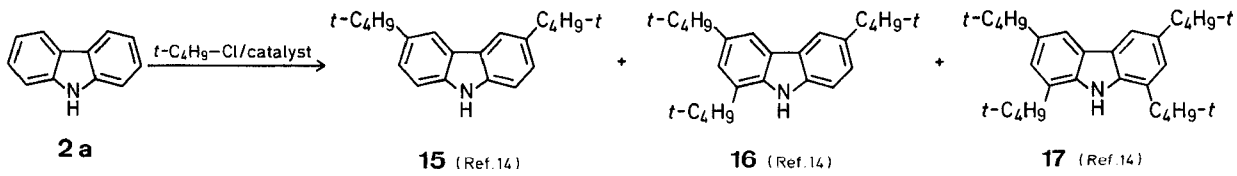
Scheme **A**



Scheme **B**

The preparations of 2-nitro-4,4'-di-*t*-butyl- (**5**), 2-nitro-4-*t*-butyl- (**8**) and 2-methyl-4,4'-di-*t*-butylbiphenyl (**11**) were described in a previous paper[1]. The nitration of **11** with fuming nitric acid afforded a mixture of 2-methyl-6-nitro- (**12**) and 2-methyl-2'-nitrobiphenyl (**13**) which could not be easily separated from each other by the usual means. On the treatment of the nitro compounds such as **5** or **8** and the mixture of **12** and **13** with triethyl phosphite under reflux, the expected carbazoles such as 2,7-di-*t*-butyl- (**6**), 2-*t*-butyl- (**9**), and 2,7-di-*t*-butyl-4-methylcarbazole (**14**), respectively were obtained.

It should be noted that the direct Friedel-Crafts *t*-butylation[14] of **2a** with *t*-butyl chloride afforded a mixture of 3,6-di-*t*-butyl- (**15**), 1,3,6-tri-*t*-butyl- (**16**), and 1,3,6,8-tetra-*t*-butylcarbazole (**17**) but not **6** and **9**.



| | | | | |
|---|---|---|---|---|
| $C_{20}H_{25}N$ | calc. | C 85.97 | H 9.02 | N 5.01 |
| (279.4) | found | 84.20 | 9.07 | 4.86 |

I.R. (KBr): $\nu_{max}$ = 3300, 2950, 1605, 1450, 1270, 805, 740 cm$^{-1}$.

$^1$H-N.M.R. ($CCl_4$): $\delta$ = 1.36 (s, 18H); 3.65 (s, 1H); 7.00–7.92 ppm (m, 6H).

**2-*t*-Butylcarbazole (9):**

A mixture of 2-nitro-4-*t*-butylbiphenyl[1] (**8**; 2.4 g, 10 mmol) and triethyl phosphite (0.6 g, 40 mmol) is treated and worked up as described above to give **9** as colorless plates; yield: 1.35 g (65%); m.p. 222–223° (from hexane).

| | | | | |
|---|---|---|---|---|
| $C_{16}H_{17}N$ | calc. | C 86.05 | H 7.67 | N 6.27 |
| (223.3) | found | 86.19 | 7.73 | 6.27 |

I.R. (KBr): $\nu_{max}$ = 3420, 3060, 2960, 1610, 1460, 1435, 1320, 1250, 820, 750, 730 cm$^{-1}$.

$^1$H-N.M.R. ($CDCl_3$): $\delta$ = 1.42 (s, 18H); 7.08–8.05 ppm (m, 7H).

**Nitration of 4,4'-Di-*t*-butyl-2-methyldiphenyl (11):**

To a solution of **11**[1] (5.30 g, 20 mmol) in acetic anhydride (100 ml) is added a solution of fuming nitric acid (d = 1.5, 5 ml) in acetic acid (30 ml) at 5–7°. After the reaction mixture has been stirred at room temperature for 1 h, it is poured into a large amount of ice/water. The organic layer is extracted with ether. The ether solution is washed with 10% sodium hydroxide solution and water, dried over sodium sulfate, and evaporated in vacuo to leave the residue which is column chromatographed on silica gel using a mixture of hexane/benzene (1:1) as an eluent to afford a mixture of **12** and **13** (40:60) as a pale yellow liquid; yield: 5 g (80%). The distribution of **12** and **13** was confirmed by liquid chromatography (conditions: Hitachi liquid chromatography, HITACHI 634, press 40 kg/cm$^2$, eluent: ethanol; column: Sus 32, temperature: 27°, cell volume 9 $\mu$l; wave length, 254 nm).

$^1$H-N.M.R. ($CCl_4$): $\delta$ = 1.38 (s, 9H); 1.43 (s, 9H); 6.92–7.50 ppm (m, 6H).

**2,7-Di-*t*-butyl-4-methylcarbazole (14):**

After a solution of the mixture **12** + **13** (4.65 g, 15 mmol) in triethyl phosphite (7.43 g, 45 mmol) has been heated under reflux for 13 h, it is treated and worked up as described above to give **14** as colorless needles; yield: 2 g (48%); m.p. 116–118° (from hexane).

| | | | | |
|---|---|---|---|---|
| $C_{21}H_{27}N$ | calc. | C 85.95 | H 9.27 | N 4.77 |
| (293.4) | found | 85.88 | 9.35 | 4.85 |

I.R. (KBr): $\nu_{max}$ = 3390, 2040, 2960, 1610, 1450, 1325, 1200, 1080, 860, 850, 815, 740 cm$^{-1}$.

$^1$H-N.M.R. ($CDCl_3$): $\delta$ = 1.39 (s, 18H); 2.50 (s, 3H); 6.78 (s, 1H); 7.14–8.03 ppm (m, 5H).

**Carbazole (2a):**

*From 2,7-di-t-butylcarbazole* (**6**): To a solution of **6**[1] (1.32 g, 5 mmol) in benzene (25 ml) is gradually added aluminum chloride (1.58 g, 12 mmol) at 50°. After the reaction mixture has been stirred for 3 h, it is quenched with ice/water. The organic layer is extracted with ether. The ether solution is washed with water, dried over sodium sulfate, and evaporated in vacuo to leave the crude product which is recrystallized from ethanol; yield: 0.75 g (90%); m.p. 244–245° (Lit.[12], m.p. 245°), colorless crystalline powder.

*From 2-t-butylcarbazole* (**9**): Similarly, **9** (1.2 g, 5 mmol) is treated and worked up as described above to afford **2a**; yield: 0.85 g (92%); m.p. 244–245°.

**4-Methylcarbazole (2b):**

Similarly 2,7-di-*t*-butyl-4-methylcarbazole (**14**: 0.278 g, 1 mmol) is treated and worked up as described above to give **2b** as colorless plates; yield: 0.14 g (77%); m.p. 120–122° (from hexane); Lit.[12], m.p. 129.5–130°.

| | | | | |
|---|---|---|---|---|
| $C_{13}H_{11}N$ | calc. | C 86.15 | H 6.12 | N 7.73 |
| (181.2) | found | 85.98 | 6.08 | 7.77 |

I.R. (KBr): $\nu_{max}$ = 3420, 3080, 1600, 1455, 1330, 780, 760, 720 cm$^{-1}$.

The formation of *t*-butylbenzene (**7**) in the aluminum chloride-catalyzed trans-*t*-butylation of **6**, **9**, and **14** in benzene was confirmed by G.L.C. (conditions: Yanagimoto gas chromatograph, YANACO YR 100; 30% high vacuum silicon grease, 75 cm; programmed temperature rise, 12°/min; carrier gas helium, 25 ml/min), respectively.

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