Sulphur Nitride in Organic Chemistry. Part 17.[1] Preparation of 1,8-Diaminocarbazole

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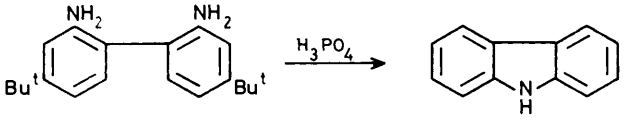
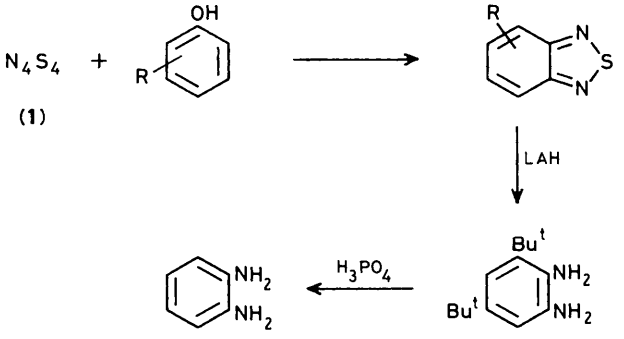
Tetrasulphur tetranitride (**1**) reacted with 5,5′-di-t-butylbiphenyl-2,2′-diol (**3a—d**) to give 4-(2-hydroxyphenyl)-2,1,3-benzothiadiazole (**4a**) and (**4c**), bi-2,1,3-benzothiadiazol-4-yl (**5**), and benzofurano[3,2-*e*]-2,1,3-benzothiadiazole (**6**), the yields of which were dependent upon the *ortho* substituent of (**3**) and an equimolar ratio of (**1**) : (**3**). Reduction of compound (**5**) with $SnCl_2$ in acetic acid–concentrated hydrochloric acid gave the imidazolyl-thiazole (**11**), while reduction with Sn in concentrated hydrochloric acid gave tetra-aminobiphenyl (**9**), which was diazotised to give the bitriazolyl (**12**). Compound (**9**) when heated in phosphoric acid give 1,8-diaminocarbazole (**2**) [27% yield from the dibromobiphenyldiol (**3c**)].

Previously, we have reported[2] the preparation of carbazole by cyclization of 2,2′-diamino-4,4′-di-t-butylbiphenyl with coincidental de-t-butylation.



Recently, we reported[1,3] the reaction of alkyl- and alkylhalogenophenols with tetrasulphur tetranitride N_4S_4 (**1**) to give 2,1,3-benzothiadiazoles. It was also reported[1] that 4,7-di-t-butyl-2,1,3-benzothiadiazole was converted into *o*-phenylenediamine on reduction and subsequent de-t-butylation.

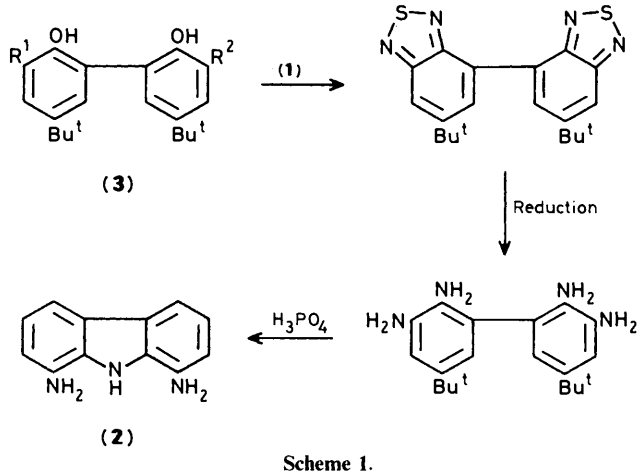


The above results, point to the possibility of preparing 1,8-diaminocarbazole (**2**) from t-butylbiphenyl-2,2′-diols (**3**) (see Scheme 1). Compound (**2**) bears an interesting array of two NH_2 groups and one carbazole NH, a rare type of heterocyclic system of which 4,5-diaminoacridine[4] is the only known example.

The results of our studies in this area of work are described herein.

Results and Discussion

Reaction of N_4S_4 (**1**) *with the Biphenyldiol* (**3**).—It was found[1,3] that in the reaction of phenols with (**1**), halogen atoms



Scheme 1.

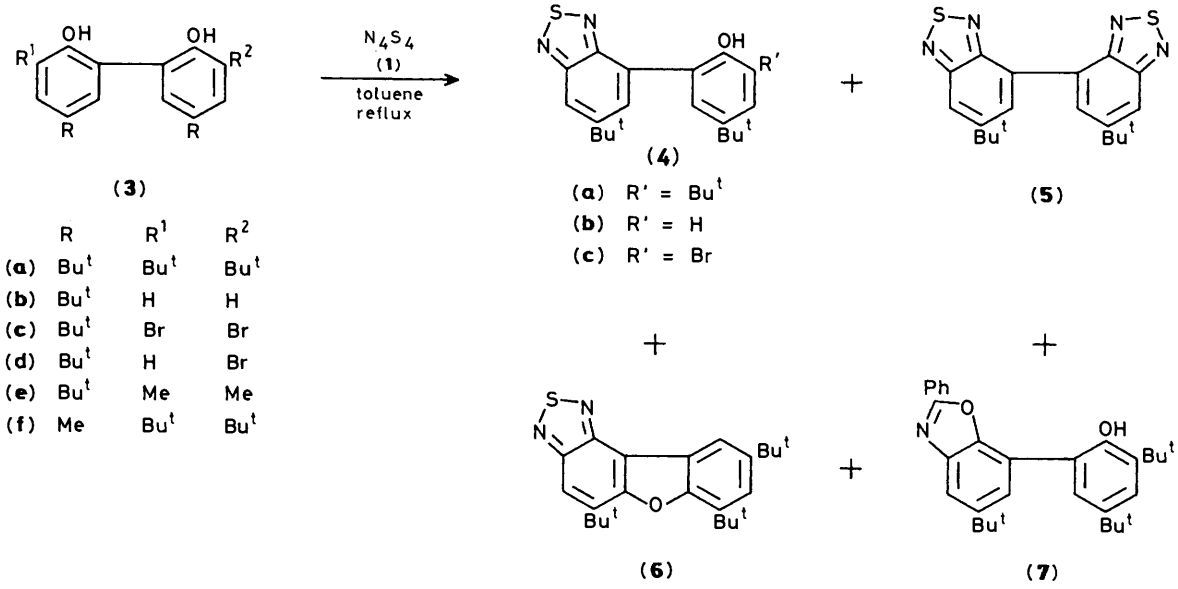
and a t-butyl group in the *ortho* position to the phenol are eliminated during the 1,2,5-thiadiazole ring formation. Thus, compound (**1**) was allowed to react with t-butyl- and t-butyl-bromo-biphenyl-2,2′-diols (**3a—d**) and the results are summarized in Scheme 2 and the Table.

The reaction of (**1**) with (**3a**) afforded (**4a**), (**5**), and (**6**), whose yields are dependent on the amount of (**1**) employed. Although use of an increased amount of (**1**) lowered the yield of (**4a**), it raised those of (**5**) and (**6**). The reaction of (**4a**) with 2 equiv. of (**1**) afforded (**5**) (18%) and (**6**) (24%), together with unchanged (**4a**) (25%); 2,4,6,8-tetra-t-butyldibenzofuran-1-ol (**8**)[5] reacted with (**1**) to give (**6**) (61%) suggesting that (**6**) is formed *via* (**8**). In the reaction of (**1**) with (**3b**), compound (**5**) was the sole product, no starting material being detected and (**4b**), the expected product, not being formed even when a single equivalent of (**1**) was used. In contrast, the expected compounds (**4c**) (8%) and (**5**) (15%) were obtained from a 24 h reaction of (**3c**) with an equimolar amount of (**1**); no starting material was recovered. With 2 equiv. of (**1**) compound (**5**) (63—72%) and benzyl bromide (14—32%) were obtained. This suggests that toluene as solvent, undergoes radical attack by bromine eliminated from (**3c**) during ring closure. Since compound (**4c**) reacted with (**1**) to give (**5**) (69%), the two 1,2,5-thiadiazole rings

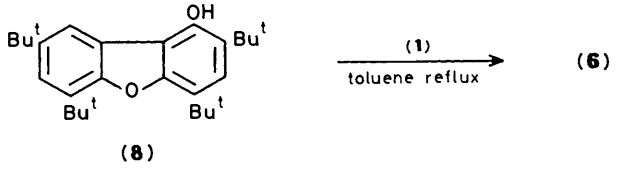
Table. Reaction of N_4S_4 (**1**) with biphenylols (**3**) and (**4**)

Substrate	(**1**)/Substrate[a]	Time (h)	Products (mol %)[b]
(**3a**)[c]	1	67	(**3a**) (14), (**4a**) (21), (**5**) (2), (**6**) (8)
(**3a**)[c]	2	67	(**4a**) (19), (**5**) (10), (**6**) (15)
(**3a**)[c]	4	67	(**4a**) (9), (**5**) (23), (**6**) (21)
(**3b**)	1	24	(**5**) (18)
(**3b**)	2	24	(**5**) (37)
(**3b**)	2	48	(**5**) (68)
(**3c**)	1	24	(**4c**) (8), (**5**) (15)
(**3c**)	2	24	(**5**) (63) $PhCh_2Br$ (14)
(**3c**)	2	48	(**5**) (72), $PhCH_2Br$ (32)
(**3d**)	1	24	(**4c**) (14), (**5**) (12)
(**3d**)	2	24	(**5**) (53)
(**4a**)	2	67	(**4a**) (25), (**5**) (18), (**6**) (24)
(**4c**)	1	24	(**5**) (69)

[a] Molar ratio. [b] Isolated yield; calculated on the basis of the substrate used. [c] A trace amount of (**7**) was obtained.



Scheme 2.



of the latter might be formed in a stepwise fashion in the reaction with (**3c**).

When a 1:1 mixture of (**1**) and the asymmetric compound (**3d**) was heated in refluxing toluene, primarily the non-bromine containing ring reacted, (**4c**) (14%) and (**5**) (12%) being formed but no (**4b**). Treatment of (**3d**) with 2 equiv. of (**1**) afforded only (**5**) (53%).

The reactions with 3,3′-dimethyl-5,5′-di-t-butyl-(**2e**)[6] and 5,5′-dimethyl-3,3′-di-t-butyl-biphenyl-2,2′-diol (**2f**)[7] gave poor results whilst (**2f**) gave only resins, and unchanged (**2e**) (32%).

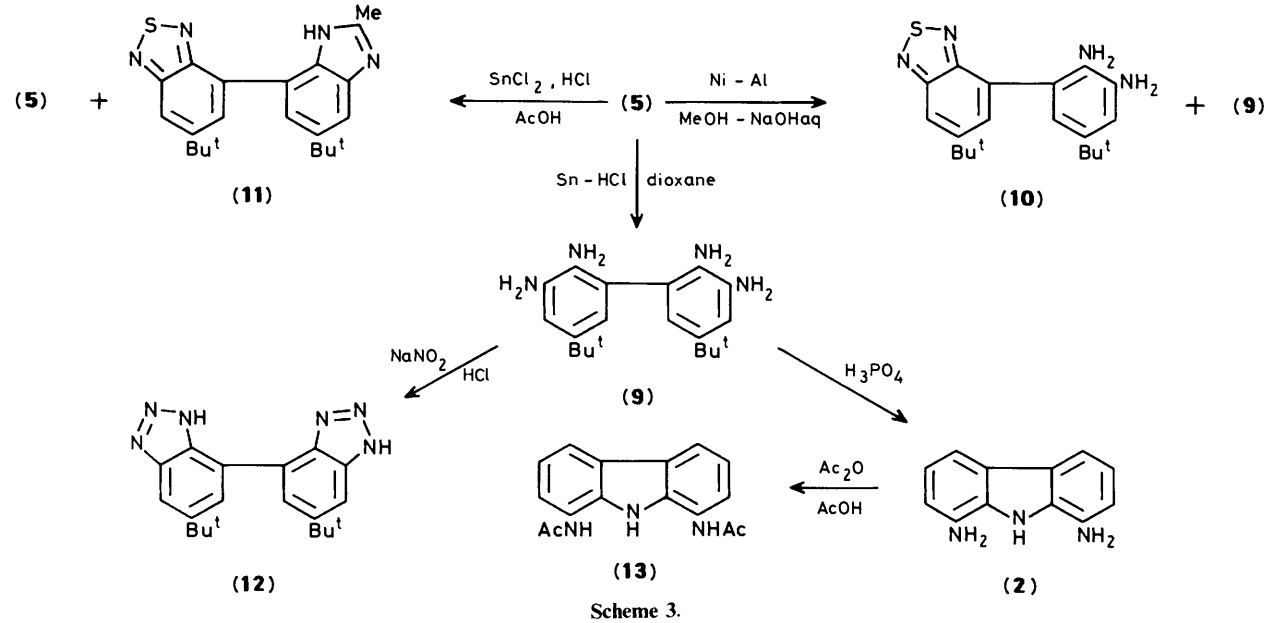
Preparation of 1,8-*Diaminocarbazole* (**2**).—Reduction of (**5**) with Raney Ni–Al alloy in methanol–aqueous NaOH gave the tetra-amine (**9**) (9%) and the diamine (**10**) (7%). In a dioxane–aqueous KOH, the reduction gave (**9**) as an unstable white solid, which, without purification, was heated in refluxing phosphoric acid to give the expected compound (**2**) [20% from (**5**)]. This procedure has the disadvantage of using large amounts of alloy and solvent (see Experimental section).

$LiAlH_4$ Reduction also gave crude compound (**9**) which was converted into (**2**) [5—15% from (**5**)].

Reduction with $SnCl_2$ in acetic acid–concentrated hydrochloric acid afforded the benzothiadiazolyl-benzoimidazole (**11**) (31%) and unchanged (**5**) (39%).

Treatment of compound (**5**) with Sn powder in dioxane–concentrated hydrochloric acid and continuous extraction of the resultant solid product with ether gave (**9**)·H_2O as white needles (88%). Diazotization of this adduct afforded the expected bibenzotriazolyl (**12**) (65%). Diaminocarbazole (**2**) was obtained (45%) by treatment of the adduct with phosphoric acid as silver-coloured prisms on recrystallization from degassed benzene.

In the ^1H n.m.r. spectrum of (**2**) in $(CD_3)_2SO$, the NH_2 and ring NH signals were observed at 4.92 and 10.32 p.p.m.; respectively. These values are similar to those of aniline and carbazole, suggesting that intramolecular NH_2/NH hydrogen bonding is absent. Solid compound (**2**) decomposed slowly and, overnight, in solution, it gave violet resins. Acetylation of



Scheme 3.

compound (**2**) with acetic anhydride gave 1,8-diacetamidocarbazole (**13**) (64%).

Experimental

M.p.s were determined on a Yanagimoto micro-melting point apparatus and Mitamura-riken MELT-THERMO and are uncorrected. Mass spectra were obtained on a Nippon Denshi JMS-01SG-2 mass spectrometer at 75 eV using a direct inlet system. N.m.r. spectra were recorded on a Nippon Denshi JEOL FT-100 and GSX-270 using $SiMe_4$ as an internal standard in $CDCl_3$ unless otherwise stated. I.r. spectra were measured on Nippon-bunko A-102 spectrophotometer as potassium bromide pellets. Column chromatography was carried out on silica gel (Wako gel, C-300).

Preparation of Compounds (**3c**) *and* (**3d**).—A solution of bromine (2.56 g, 16 mmol) in methanol (20 ml) was added dropwise to a solution of (**3b**)[8] (40 ml) at 0—5 °C during 1 h. After the addition, the mixture was poured into a large volume of water and the precipitated solid was filtered off. Column chromatography of the solid with methylene dichloride as eluant afforded compounds (**3c**) (2.50 g, 68%) and (**3d**) (0.18 g, 6%), both of which were recrystallized from hexane.

Compound (**3b**) (11.49 g, 40 mmol) in methanol (350 ml) was treated with bromine (6.39 g, 40 mmol) in methanol (50 ml) as described above to give (**3c**) (2.45 g, 13%) and (**3d**) (4.71 g, 31%).

3,3′-Dibromo-5,5′-di-t-butylbiphenyl-2,2′-diol (**3c**): colourless prisms, m.p. 180—184 °C; δ 1.30 (s, 18 H), 5.78 (s, D_2O-exchanged, 2 H), 7.18 (d, *J* 2.5 Hz, 2 H), and 7.50 (d, *J* 2.5 Hz, 2 H); *m/z* 458 (M^+), 456 (M^+), 454 (M^+), 443, 441, and 439 (Found: C, 52.7; H, 5.1. $C_{20}H_{24}Br_2O_2$ requires C, 52.65; H, 5.30%).

3-Bromo-5,5′-di-t-butylbiphenyl-2,2′-diol (**3d**): colourless prisms, m.p. 191—193 °C; δ 1.30 (s, 9 H), 1.32 (s, 9 H), 5.80 and 5.94 (each s, D_2O-exchanged, 1 H), 6.94 (d, *J* 8.2 Hz, 1 H), 7.23 (d, *J* 2.2 Hz, 1 H), 7.26 (d, *J* 2.5 Hz, 1 H), 7.34 (dd, *J* 8.2 and 2.2 Hz, 1 H), and 7.53 (d, *J* 2.5 Hz, 1 H); *m/z* 378 (M^+), 376 (M^+), 363, and 361 (Found: C, 63.75; H, 6.8. $C_{20}H_{25}BrO_2$ requires C, 63.66; H, 6.68%).

Reaction of N_4S_4 (**1**) *with Compound* (**3a**).—A mixture of (**3a**) (4.92 g, 12 mmol) and an appropriate amount of (**1**) in toluene (50 ml) was refluxed for the reaction time given in the Table. The solvent was evaporated under reduced pressure and the residue was washed with chloroform and insoluble materials were filtered off. The filtrate was concentrated and then chromatographed. Sulphur and (**3a**) were eluted with hexane, (**4a**) and (**6**) with hexane–benzene (1:1), and (**5**) and (**7**) with benzene.

4-(2-Hydroxy-3,5-di-t-butylphenyl)-6-t-butyl-2,1,3-benzothiadiazole (**4a**): light yellow prisms, m.p. 159.5—160.5 °C [from water–methanol (1:8)]; δ 1.36 (s, 9 H) 1.45 (s, 9 H), 1.51 (s, 9 H), 6.71 (s, 1 H, D_2O-exchanged), 7.22 (d, *J* 2.5 Hz, 1 H), 7.46 (d, *J* 2.5 Hz, 1 H), 7.76 (d, *J* 1.5 Hz, 1 H), and 7.90 (d, *J* 1.5 Hz, 1 H); *m/z* 396 (M^+), 381, and 325 (Found: C, 72.45; H, 8.2; N, 7.15. $C_{24}H_{32}N_2OS$ requires C, 72.68; H, 8.13; N, 7.07%).

6,6′-Di-t-butylbi-2,1,3-benzothiadiazol-4-yl (**5**): pale yellow prisms, m.p. 204—205 °C (from hexane); δ 1.50 (s, 18 H), 7.95 (d, *J* 1.9 Hz, 2 H), and 8.47 (d, *J* 1.9 Hz, 2 H); *m/z* 382 (M^+) and 367 (Found: C, 62.8; H, 5.8; N, 14.65. $C_{20}H_{22}N_4S_2$ requires C, 62.79; H, 5.80; N, 14.65%).

5,7,9-Tri-t-butylbenzofurano[3,2-*e*]-2,1,3-benzothiadiazole (**6**): pale yellow prisms, m.p. 157—158.5 °C; δ 1.49 (s, 9 H), 1.65 (s, 9 H), 1.67 (s, 9 H), 7.49 (d, *J* 2 Hz, 1 H), 7.84 (s, 1 H), and 8.33 (d, *J* 2 Hz, 1 H); *m/z* 394 (M^+), 379, and 256 (Found: C, 73.25; H, 7.75; N, 7.3. $C_{24}H_{30}N_2OS$ requires C, 73.06; H, 7.66; N, 7.10%).

7-(2-Hydroxy-3,5-di-t-butylphenyl)-2-phenyl-5-t-butylbenzoxazole (**7**): white needles, m.p. (in sealed tube) 240.5—241.5 °C (from light petroleum); δ 1.37 (s, 9 H), 1.43 (s, 9 H), 1.50 (s, 9 H), 5.36 (s, 1 H, D_2O-exchanged), 7.30 (d, *J* 2 Hz, 1 H), 7.4—7.5 (m, 5 H), 7.81 (d, *J* 2 Hz, 1 H), and 8.1—8.2 (m, 2 H); *m/z* 455 (M^+), 440, and 384 (Found: C, 81.3; H, 8.2; N, 3.3. $C_{31}H_{37}NO_2$ requires C, 81.72; H, 8.19; N, 3.07).

Reaction of N_4S_4 (**1**) *with Compound* (**3b**).—A mixture of compound (**3b**) (2.39 g, 8 mmol) and an appropriate quantity of (**1**) in toluene (40 ml) was treated as described above to give compound (**5**).

Reaction of N_4S_4 (**1**) *with Compound* (**3c**).—A mixture of compound (**3c**) (1.37 g, 3 mmol) and an appropriate quantity of (**1**) was treated as described above, and, on chromatography, gave benzyl bromide with hexane as eluant and (**4c**) and/or (**5**) with benzene as eluant.

4-(3-Bromo-2-hydroxy-5-t-butylphenyl)-6-t-butyl-2,1,3-benzothiadiazole (**4c**): pale yellow prisms, m.p. 114.5—117 °C [from water–ethanol (1:7)]; δ 1.34 (s, 9 H), 1.44 (s, 9 H), 6.40 (s, 1 H, D_2O-exchanged), and 7.44, 7.58, 7.78, and 7.90 (each d, *J* 2 Hz, 1 H); *m/z* 420 (M^+), 405, 418 (M^+), and 403 (Found: C, 57.45; H, 5.65; H, 5.65: N, 6.6. $C_{20}H_{23}BrN_2OS$ requires C, 57.28; H, 5.53; N, 6.68%).

Reaction of N_4S_4 (**1**) *with Compound* (**3d**).—A mixture of (**3d**) (0.45 g, 1.2 mmol) and an appropriate amount of (**1**) in toluene (15 ml) was treated as described above to afford (**4c**) and/or (**5**).

Reaction of N_4S_4 (**1**) *with Compound* (**4a**).—A mixture of (**1**) (0.74 g, 4 mmol) and (**4a**) (0.79 g, 2 mmol) in toluene (30 ml) was refluxed and treated as described above to give (**4a**) (0.20 g, 25%), (**5**) (0.14 g, 18%), and (**6**) (0.19 g, 24%).

Reaction of N_4S_4 (**1**) *with Compound* (**4c**).—A mixture of (**1**) (0.13 g, 0.7 mmol) and (**4c**) (0.29 g, 0.7 mmol) in toluene (10 ml) was refluxed and treated as described above to give (**5**) (0.18 g, 69%).

Reaction of N_4S_4 (**1**) *with Compound* (**8**).—A mixture of (**1**) (450 mg, 2.45 mmol) and (**8**) (1.00 g, 2.45 mmol) in toluene (20 ml) was refluxed for 18 h and treated as described above to give (**6**) (0.59 g, 61%).

Reduction of Compound (**5**).—*With Raney* Ni–Al *alloy*. Raney Ni–Al alloy (11 g) was added in small portions to a mixture of compound (**5**) (1.15 g) and sodium hydroxide (11 g) in ethanol (250 ml), and the mixture was stirred at ambient temperature for 2 h; it was then poured into water (800 ml). The mixture was filtered, the filtrate extracted with benzene (300 ml), and the extract dried ($MgSO_4$) and concentrated under reduced pressure to *ca.* 15 ml. Chromatography of this using ethyl acetate as eluant, gave (**9**) (98 mg, 9%) and (**10**) (77 mg, 7%). Compound (**9**) was unstable and easily decomposed in air to give a violet tar. An analytical sample of (**9**) was obtained by reduction with Sn and concentrated hydrochloric acid (see later).

4-(2,3-Diamino-5-t-butylphenyl)-6-t-butyl-2,1,3-benzothiadiazole (**10**): yellow prisms, m.p. 202—205 °C (from hexane); ν(NH) 3 400 and 3 350 cm^{-1}; δ 1.24 (s, 9 H), 1.42 (s, 9 H), 6.83 (s, 2 H), 7.66 (d, *J* 2.0 Hz, 1 H), and 7.85 (d, *J* 2.0 Hz, 1 H); *m/z* 355 (*M* + 1) (Found: C, 67.55; H, 7.35; N, 15.55. $C_{20}H_{26}N_4S$ requires C, 67.76; H, 7.39; N, 15.80%).

With $LiAlH_4$: *typical procedure*. Compound (**5**) (380 mg, 1 mmol) in dry dioxane (25 ml) was added dropwise at 0 °C under a nitrogen atmosphere to a stirred mixture of $LiAlH_4$ (230 mg, 6 mmol) in dry dioxane (30 ml), and the mixture was refluxed for 3 h. Ethyl acetate (2 ml) and then water (5 ml) were added to the mixture which was then filtered. The filtrate was poured into cold water (200 ml), extracted with benzene (100 ml × 2), and the extract dried ($MgSO_4$) and evaporated under reduced pressure to afford crude (**9**). This, without purification, was heated in phosphoric acid (30 ml) for 15 h and treated as will be described later in the reduction with Sn to give (**2**) (28.8 mg, 15%).

With $SnCl_2$. A mixture of compound (**5**) (1.15 g, 3 mmol), $SnCl_2$ (2.6 g, 13.7 mmol), and concentrated hydrochloric acid (5 ml) in acetic acid (15 ml) was refluxed for 6 h after which it was poured into water (150 ml) and extracted with ether (100 ml × 2). The extract was washed with water, 30% aqueous sodium hydrogen carbonate, and water, and evaporated under reduced pressure to give a residue. This, on chromatography with benzene as an eluant, afforded unchanged (**5**) (450 mg, 39%) and (**11**) (355 mg, 31%). 4-(2-Methyl-6-t-butylbenzimidazol-4-yl)-6-t-butyl-2,1,3-benzothiadiazole (**11**): colourless prisms, m.p. 258—260.5 °C (from hexane); ν(NH) 3 450 cm^{-1}; δ 1.44 (s, 9 H), 1.46 (s, 9 H), 2.48 (s, 3 H), 7.57 (d, *J* 2.0 Hz, 1 H), 7.76 (d, *J* 2.0 Hz, 1 H), 7.95 (d, *J* 2.0 Hz, 1 H), and 7.98 (d, *J* 2.0 Hz, 1 H); *m/z* 378 (M^+) (Found: C, 69.5; H, 7.0; N, 14.3. $C_{22}H_{26}N_4S$ requires C, 69.81; H, 6.92; N, 14.80%).

With Sn. 12M Hydrochloric acid (50 ml) was added in one portion with vigorous stirring to a warmed mixture of (**5**) (5.0 g, 13.1 mmol) and powdered tin (15.5 g, 131 mmol) in dioxane (150 ml) and the mixture was refluxed for 3 h. It was then poured onto ice–water (300 ml) and neutralized with sodium hydrogen carbonate. The precipitate was filtered off and continuously extracted with ether (250 ml) overnight in a Soxhlet apparatus; this afforded (**9**)·H_2O (3.96 g, 88%) as colourless needles, m.p. 109—115 °C, which was dehydrated overnight under reduced pressure (2 mmHg) at 110—120 °C to give pure 2,2′,3,3′-tetra-amino-5,5′-di-t-butylbiphenyl (**9**): colourless needles, m.p. 203—206 °C (from ether); ν(NH) 3 400 and 3 350 cm^{-1}; δ ($CDCl_3$ + CD_3SOCD_3) 1.27 (s, 18 H), 3.69 (br, s, 8 H), 6.46 (d, *J* 2.2 Hz, 2 H), and 6.69 (d, *J* 2.2 Hz, 2 H); *m/z* 326 (M^+) and 311 (Found: C, 73.5; H, 9.25; N, 17.2. $C_{20}H_{30}N_4$ requires C, 73.58; H, 9.26; N, 17.16%).

Diazotization of Compound (**9**).—Compound (**9**)·H_2O (1.3 g, 3.77 mmol) in a mixture of 12M hydrochloric acid (15 ml), water (85 ml), and ethanol (60 ml) was diazotized in an ice–water bath by dropwise addition of sodium nitrite (540 mg, 7.83 mmol) in water (5 ml); it was then stirred at this temperature for 0.5 h. After this, the ice–water bath was removed and the mixture was stirred at room temperature for 1 h. Precipitated 6,6′-di-t-butylbibenzotriazol-4-yl (**12**) (858 mg, 65%) was filtered off and recrystallized from ethanol to afford pale yellow prisms, m.p. 298—300 °C; $\delta_H(CD_3SOCD_3)$ 1.48 (s, 18 H), 7.79 (br s, 4 H), and 9.08 (br s, 2 H); $\delta_C(CD_3SOCD_3)$ 31.3, 35.1, 106.1, 124.7, 127.0, 134.3, 141.2, and 150.4; *m/z* 348 (M^+), 304, and 78 (Found: C, 68.95; H, 6.95; N, 24.5. $C_{20}H_{24}N_6$ requires C, 68.94; H, 6.94; N, 24.12%).

Preparation of Compound (**2**).—A mixture of compound (**9**)·H_2O (300 mg, 9.20 mmol) in phosphoric acid (15 ml), which was degassed with nitrogen for 1 h before use, was stirred under refluxed for 8 h with passage of nitrogen and then poured into water (200 ml). It was neutralized with sodium hydrogen carbonate and extracted with ether (150 ml × 2). The ether extract was concentrated to afford 1,8-diaminocarbazole (**2**) (77 mg, 45%): silver-coloured plates, m.p. 230 °C (decomp.) (from benzene); ν(NH_2) 3 400, 3 380, and 3 320 cm^{-1}; δ (CD_3SOCD_3) 4.92 (br s, 4 H), 6.60 (dd, *J* 7.5 and 1.0 Hz, 2 H), 6.84 (dd, *J* 7.5 and 7.5 Hz, 2 H), 7.24 (dd, *J* 7.5 and 1.0 Hz, 2 H), and 10.32 (br s, 1 H); *m/z* 197 (M^+) (Found: C, 72.85; H, 5.6; N, 21.2. $C_{12}H_{11}N_3$ requires C, 73.07; H, 5.62; N, 21.30).

Acetylation of Compound (**2**).—A mixture of compound (**2**) (75 mg, 3.80 mmol), acetic anhydride (2 ml), and glacial acetic acid (6 ml) was stirred at room temperature for 2 h after which precipitated 1,8-diacetamidocarbazole (**13**) (67 mg, 64%) was filtered off: colourless needles, m.p. 320–322 °C (decomp.) (from ethanol); ν(NH) 3 500 and 3 280 and ν(CO) 1 680 cm^{-1}; $\delta_H(CD_3SOCD_3)$ 2.18 (s, 6 H), 7.18 (dd, *J* 4.0 and 4.0 Hz, 2 H), 7.56 (d, *J* 4.0 Hz, 2 H), 7.88 (d, *J* 4.0 Hz, 2 H), 10.00 (br s, 2 H), and 10.24 (br s, 1 H); $\delta_C(CD_3SOCD_3)$ 23.5, 116.4, 118.9, 119.1, 123.0, 124.1, 132.2, and 168.4; *m/z* 281 (M^+), 239, 221, 197, and 196 (Found: C, 68.4; H, 5.4; N, 14.7. $C_{16}H_{15}N_3O_2$ requires C, 68.31; H, 5.37; N, 14.94%).

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