New Synthesis of Diarylalkynes from 1-(Arylmethyl)benzotriazoles and Arylideneamines

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The Michael addition of lithio derivatives **2** of 1-(arylmethyl)benzotriazoles **1** to arylideneamines **3–5** gave the corresponding 1-(benzotriazol-1-yl)-2-anilino (or tosylamino)-1,2-diarylethanes **6–8**. The latter were shown to undergo a double elimination reaction under the action of Bu^{t}OK in DMF to afford diarylalkynes in high yields.

Previous publications from our laboratory have shown that transformations of benzotriazole-stabilized carbanions enable the convenient preparation of aromatic ketones,[1] carboxylic acids,[2] aldehydes[3] and other derivatives.[4,5] Recently, we reported a new synthesis for 1-(arylmethyl)benzotriazoles and some novel transformations of the corresponding benzotriazol-1-yl carbanions.[6] We now disclose the first examples of reactions of metallated 1-(arylmethyl)benzotriazoles with arylideneamines and their use for the preparation of diarylalkynes.

Results and Discussion

Reactions of Lithiated 1-(arylmethyl)benzotriazoles **2** *with Arylideneamines* **3**.—The lithiated 1-(arylmethyl)benzotriazoles **2a, b**, generated *in situ* by the action of LDA on the compounds **1a, b** in THF,[6] reacted smoothly with arylideneamines **3–5** to give the corresponding 1-(benzotriazol-1-yl)-2-anilino (or tosylamino)-1,2-diarylethanes **6–8** in high yields (Scheme 1).

The structures of compounds **6–8** were supported by elemental analyses and spectral data. Isolated products **8a** and **8b** appeared to be diastereoisomerically pure, whereas compounds **6a, b** and **7** were obtained as mixtures of two diastereoisomers in ratios of 1:2, 1:2 and 1:2.6, respectively. The major diastereomers of **6a, b** and **7** were isolated by recrystallization from methanol.

The ^{1}H NMR spectra of the products **6–8** in $(CD_3)_2SO$ displayed doublets for the benzotriazole 4-H protons at δ 7.80–8.09 (*cf.* ref. 7, J 8.1–8.4 Hz). Vicinal 2-H and 1-H protons resonated at δ 5.62–6.01 and 6.15–6.43, respectively. The latter signals in the spectra of **8a, b** overlapped the resonances of the aromatic CH and NH protons. The NH signals in the spectra of **6a, b** and **7** appeared at δ 8.36–8.60. These assignments were confirmed by deuterium-exchange experiments. Thus, in the spectrum of **8b** in $(CD_3)_2SO$–CD_3OD, the 2-H signal, initially observed in $(CD_3)_2SO$ as a doublet of doublets at δ 6.01 (J 10.1 and 10.2), is converted after deuteriation into a doublet (J 10.2), whereas the 3H-multiplet at δ 6.30–6.46 is transformed into a doublet of doublets at δ 7.16 (1 H, J 7.3 and 7.6 Hz, arom. CH) and a doublet at δ 6.33 (1 H, J 10.2 Hz, 1-H). The ^{13}C NMR spectra of compounds **6–8** displayed C-1 and C-2 signals (APT experiments) at δ 65.5–67.0 and 55.3–60.5, respectively, along with the expected number of aromatic signals.

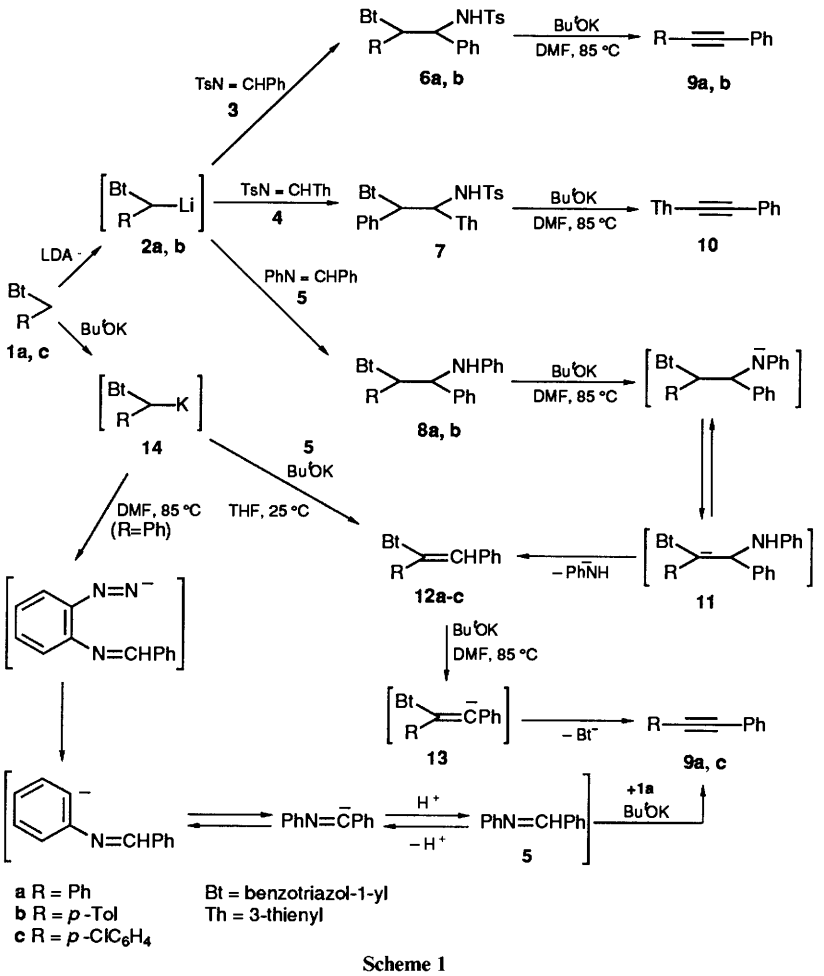
Transformations of 1-(*Benzotriazol-1-yl*)-2-*anilino*(*or tosylamino*)-1,2-*diarylethanes* **6–8** *into Diarylalkynes* **9, 10**.—Compounds **6–8** with Bu^{t}OK in DMF at 85 °C gave the diarylalkynes **9, 10** (Scheme 1). Optimal yields of these products (75–84%) were achieved using 1,2-diamines **6a, b, 7** or **8a** and Bu^{t}OK in the molar ratio of 1:4.

Conversions of the 2-anilinoethanes **8a, b** under the reaction conditions were significantly faster then those of the 2-tosylamino-derivatives **6a, b** and **7**: the observed times for the completion of the processes were *ca.* 10 or 40 min, respectively (the reactions were monitored by TLC for the disappearance of starting compounds **6–8**). This difference probably reflects the easier reversible formation of anionic species **11** in the case of **8a, b** due to the lower acidity of the anilino substituent in comparison with the tosylamino group (Scheme 1). Intermediates **11** evidently eliminate anilino anion to afford enamines **12**, these then lose a proton under the reaction conditions to give anions **13**, which spontaneously eliminate benzotriazole anion yielding diarylalkynes **9**. Indeed, compounds **8a, b** were found to give enamines **12a, b** under the action of NaH in DMF at 80 °C in 60 and 40% yields respectively. Significantly, in the reaction of **8b** with NaH 1-(*p*-tolymethyl)benzotriazole **1b** was also isolated in 20% yield indicating the retro-fission of **8b** under the reaction conditions (*cf.* ref. 8: Michael addition is known to be a reversible process). Analogous schemes can be suggested for the transformations of **6, 7** into **9, 10**.

Furthermore, we have found that enamines **12a–c** can be easily prepared by condensation of 1-(arylmethyl)benzotriazoles **1a–c** with benzylideneaniline **5** in the presence of Bu^{t}OK in THF at 25 °C. Compounds **12a, c** on the action of Bu^{t}OK in DMF at 85 °C gave diarylalkynes **9a** and **9c** in 83 and 70% yields, respectively.

Recently, the condensation of *N*-aryl(or alkyl)-*N*-benzylanilines (including 5-benzylcarbazole) with benzylideneaniline was reported to give enamines in good yields when heated in DMF in the presence of an excess of Bu^{t}OK,[9] and no formation of alkynes was reported in this process. However, in our hands 1-(arylmethyl)benzotriazoles **1a, c** reacted with benzylideneaniline **5** and Bu^{t}OK in DMF at 85 °C to give alkynes **9a, d** in 80 and 40% yields, respectively. In general, enamines are known to be stable towards the action of bases, although a few examples of elimination reactions of quaternized enamines under pyrolytic[10] or basic conditions[11,12] have been reported to give acetylene derivatives. A similar cleavage of enamines containing an unsubstituted amino group was achieved by heating with isopentyl nitrite.[13]

This unusual reactivity of enamines **12** towards the action of Bu^{t}OK in DMF can be attributed both to the π-deficient character of the benzotriazole ring, which provides the necessary acidity of the β-olefinic proton, and to the relatively high acidity of benzotriazole (pK_a *ca.* 8), which makes the scission of intermediates **13** (Scheme 1) a thermodynamically favourable process. However, the reaction of compound **8b** with Bu^{t}OK, as well as the transformation of **1b** and **5** under similar conditions (Scheme 1) gave only low yields of the alkyne **9b** (10–15% after column chromatography; no detailed study of



Scheme 1

the reaction mixtures was carried out). Thus, the process using (*N*-tosyl)arylideneimines **3** and **4** *via* the corresponding 1,2-diamines **6**, **7** provides a more general route to diarylalkynes **9**, **10**. Attempted direct syntheses of alkynes from compounds **1a**, **b** by reaction with **3**, **4** in the presence of Bu'OK in DMF did not give satisfactory results. However, a one-pot procedure can be applied to the preparation of diarylalkynes **9**, **10** *via* compounds **6**–**8** (see Experimental section).

The structures of compounds **12**, **9** and **10** were supported by spectral data and (for **9a–c**) by comparison with reported m.p.s (see Experimental section). The ^{13}C NMR spectra of diarylalkynes **9**, **10** displayed the characteristic signals for the acetylenic carbons in the region δ 84.5–90.3.

Recently it was shown in our laboratory[6,14] that benzotriazol-1-yl carbanions can undergo cleavage with subsequent loss of nitrogen and formation of *o*-carbiminophenyl anions followed by arylideneanilines. The deep blue solutions of our lithiated 1-(arylmethyl)benzotriazoles **2a**, **b** in THF were also found to lose nitrogen above −20 °C.[6] By contrast, the THF solutions of compounds **1a**, **b** in the presence of Bu'OK were colourless and did not change at 25 °C over *ca.* 48 h (complete recovery of starting compounds was possible). However, as already mentioned, the **1a**, **b**–Bu'OK system was reactive towards benzylideneaniline **5**, indicating the presence of metallated species **14** in the reaction media (*cf.* ref. 15: reactions of CH acids with arylideneamines require the generation of the derived carbanions). This behaviour probably reflects a stabilizing effect of Bu'OK on the metallated 1-(arylmethyl)benzotriazoles **14** due to solvation (*cf.* ref. 16: the ability of polar solvents to influence the reactivity of the metal derivatives of weak CH-acids has long been recognized). When compound **1a** was heated with Bu'OK in DMF at 85 °C, nitrogen was evolved, and diphenylacetylene **9a** was isolated in 22% yield. This new benzotriazole ring fragmentation probably occurs by the intermediate formation of benzylideneaniline **5** (*cf.* ref. 6) and its condensation with more **1a** in the presence of Bu'OK.

In spite of numerous known approaches to acetylenes,[17] dehydrohalogenation of various dihalogenoethane and halogenoethene derivatives remains the most common synthetic method.[17–20] A number of syntheses of disubstituted alkynes have recently been reported (1) by the reductive elimination reaction of 2-benzenesulfonylvinylphosphates,[21] (2) from nitrimines,[22] (3) by the reaction of diazomethyltrimethylsilane[23] or dialkyl diazomethyl phosphonates[23,24] with carbonyl compounds, (4) by the oxidation of dihydrazones of α-diketones,[25,26] (5) by flash vacuum pyrolysis of β-oxoalkylidenephosphoranes,[27] (6) from lithium (1-alkynyl)organoborates[28] and (7) by the elimination of 1-arylsulfonyl-2-acetoxyethanes.[29] Preparation of aryl- or heteroaryl-acetylenes from aryl or heteroaryl halides and terminal acetylenes in the presence of $Pd(PPh_3)Cl_2$ and CuI was patented.[30]

To our knowledge, no preparation of alkynes by the base-assisted double elimination reaction of 1,2-diamines has been reported previously. The closest literature analogy to our new reaction of 1,2-diamines **6**–**8** is the transformation of 1,2-di(trimethylammonio)ethane dibromide into acetylene by KOH.[31]

The presently described synthesis of diarylalkynes from readily available 1-(arylmethyl)benzotriazoles **1** and arylideneamines **3**–**5** *via* 1,2-diamines **6**–**8** provides a new and convenient general route to these derivatives. The method enables a one-pot procedure and does not require the use of highly reactive

and toxic halogens or hydrogen halides. The further development of synthetic methods based on the new Michael addition of benzotriazol-1-yl carbanions to imines and related compounds is in progress in our laboratory.

Experimental

M.p.s were determined on a Fisher-Johns hot-stage apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian XL300 or General Electric QE300 spectrometer (300 and 75 MHz, respectively) in $(CD_3)_2SO$ (for compounds **6a**, **b** and **7**) or $CDCl_3$ referenced to Me_4Si for the proton spectra and the solvent for the carbon spectra. Elemental analyses were performed on a Carlo Erba 1106 elemental analyser. Tetrahydrofuran was distilled under nitrogen from sodium/benzophenone immediately before use. All reactions with water-sensitive compounds were carried out under dry nitrogen atmospheres. 1-(Arylmethyl)benzotriazoles **1** were prepared according to a literature procedure.[32]

General Procedure for the Preparation of 1-(*Benzotriazol*-1-*yl*)-2-*anilino*-(*or tosylamino*)-1,2-*diarylethanes* **6–8**.—LDA (1.5 mol dm^{-3} solution in cyclohexane; 2.94 cm^3, 4.40 mmol) was added dropwise to a stirred solution of the appropriate compound **1** (4.00 mmol) in THF (20 cm^3) at −78 °C. After 15 min the corresponding arylideneamine **3–5** (4.40 mmol) in THF (6 cm^3) was added at −78 °C. The mixture was allowed to warm to 25 °C over *ca.* 4 h after which 20 cm^3 of 10% aqueous NH_4Cl (for **8a**, **b**) or water (for **6a**, **b**, **7**) was added; the mixtures were then extracted with $CHCl_3$ (4 × 40 cm^3). The combined extracts were washed with water (3 × 30 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The crude products **8a**, **b** were washed with hexanes (4 × 15 cm^3) whilst **6a**, **b** and **7** were washed first with diethyl ether (2 × 10 cm^3) and then hexanes (3 × 15 cm^3) to yield the pure compounds.

1-(*Benzotriazol*-1-*yl*)-2-*tosylamino*-1,2-*diphenylethane* **6a**. Yield 1.65 g (88%, a mixture of the two diastereoisomers in a 1:2 ratio). The pure major diastereoisomer was isolated by recrystallization from methanol: isolated yield 0.75 g (40%), m.p. 278–280 °C (Found: C, 68.85; H, 5.0; N, 11.8. $C_{27}H_{24}N_4O_2S$ requires C, 69.21; H, 5.16; N, 11.96%); δ_H 2.23 (3 H, s, Me), 5.64 (1 H, m, 2-H), 6.23 (1 H, m, 1-H), 6.80–7.78 (17 H, m), 7.81 (1 H, d, *J* 8.3, 4-H Bt) and 8.60 (1 H, m, NH); δ_C 20.81 (Me), 59.79 (C-2), 65.52 (C-1), 109.83 (C-7 Bt), 119.04 (C-4 Bt), 123.91 (C-5 Bt), 125.78, 126.10, 127.39, 127.72, 127.90, 128.11, 128.40, 128.53, 128.62, 128.88, 132.30 (C-7a Bt), 138.07, 141.52 and 144.34 (C-3a Bt).

1-(*Benzotriazol*-1-*yl*)-2-*tosylamino*-1-(p-*tolyl*)-2-*phenylethane* **6b**. Yield 1.79 g (93%, a mixture of the two diastereoisomers in a 1:2 ratio). The pure major diastereoisomer was isolated by recrystallization from methanol: isolated yield 0.91 g (47%), m.p. 264–265 °C (Found: C, 69.45; H, 5.4; N, 11.5. $C_{28}H_{25}N_4O_2S$ requires C, 69.83; H, 5.23; N, 11.63%); δ_H 2.24 (3 H, s, Me), 2.26 (3 H, s, Me), 5.62 (1 H, br d, *J* 11.2, 2-H), 6.15 (1 H, d, *J* 11.2, 1-H), 6.81–7.26 (12 H, m), 7.38 (1 H, dd, *J* 8.3 and 7.5, 5-H Bt), 7.57 (2 H, *J* 8.0), 7.69 (1 H, d, *J* 8.3, 7-H Bt), 7.80 (1 H, d, 8.3, 4-H Bt) and 8.60 (1 H, br s, NH); δ_C 20.70 (Me), 20.83 (Me), 59.85 (C-2), 65.26 (C-1). 109.82 (C-7 Bt), 118.89 (C-4 Bt), 123.88 (C-5 Bt), 126.06, 127.05, 127.33, 127.53, 128.30, 128.82, 128.86, 128.95, 132.25 (C-7a Bt), 133.40, 137.71, 138.17, 138.34, 141.74 and 144.34 (C-3a Bt).

1-(*Benzotriazol*-1-*yl*)-2-*tosylamino*-2-(3-*thienyl*)-1-*phenylethane* **7**. Yield 1.61 g (85%, a mixture of the two diastereoisomers in a 1:2.6 ratio). The pure major diastereoisomer was isolated by recrystallization from methanol: isolated yield 0.80 g (42%) (Found: C, 63.05; H, 4.6; N, 11.7. $C_{25}H_{22}N_4O_2S_2$ requires C, 63.27; H, 4.67; N, 11.81%); δ_H 2.25 (3 H, s, Me), 5.78 (1 H, m, 2-H), 6.16 (1 H, d, *J* 11.2, 1-H), 6.82–7.80 (15 H, m), 7.86 (1 H, *J* 8.4, 4-H Bt) and 8.47 (1 H, m, NH); δ_C 20.88 (Me), 55.31 (C-2), 65.60 (C-1), 109.91 (C-7 Bt), 118.97 (C-4 Bt), 123.23 (C-5 Bt), 123.99, 125.73, 126.11, 127.43, 128.45, 128.57, 128.93, 132.43 (C-7a Bt), 136.42, 138.09, 138.79, 141.91 and 144.41 (C-3a Bt).

2-*Anilino*-1-(*benzotriazol*-1-*yl*)-1,2-*diphenylethane* **8a**. Yield 1.40 g (90%), m.p. 225–227 °C (from acetone) (Found: C, 80.1; H, 5.7; N, 14.4. $C_{26}H_{22}N_4$ requires C, 79.97; H, 5.68; N, 14.35%); δ_H 6.01 (1 H, dd, *J* 10.0 and 10.0, 2-H), 6.43–6.33 (3 H, m, NH, 1-H and H arom.), 6.60 (2 H, d, *J* 8.0, *o*-H Ph), 6.89–7.19 (8 H, m), 7.33–7.57 (6 H, m), 8.01 (1 H, d, *J* 8.3, 7-H Bt) and 8.08 (1 H, d, *J* 8.4, 4-H Bt); δ_C 59.26 (C-2), 67.02 (C-1), 111.05 (C-7 Bt), 113.08, 116.18, 118.99 (C-6 Bt), 123.95 (C-5 Bt), 127.01, 127.80 (C-6 Bt), 127.96, 128.05, 128.10, 128.22, 128.54, 128.63, 133.17 (C-7a Bt), 136.98, 140.40, 144.98 (C-3a Bt) and 147.26.

1-(*Benzotriazol*-1-*yl*)-2-*anilino*-1-(p-*totyl*)-2-*phenylethane* **8b**. Yield 1.37 g (85%), m.p. 175–177 °C (from methanol) (Found: C, 80.4; H, 5.9; N, 13.8. $C_{27}H_{24}N_4$ requires C, 80.17; H, 5.98; N, 13.85%); δ_H 2.11 (3 H, s, Me), 6.01 (1 H, dd, *J* 10.1 and 10.2, 2-H), 6.30–6.46 (3 H, m, NH, 1-H and H arom.), 6.60 (2 H, d, *J* 8.3, *o*-H Ph), 6.90–7.55 (13 H, m), 8.00 (1 H, d, *J* 8.3, 7-H Bt) and 8.07 (1 H, d, *J* 8.2, 4-H Bt); δ_C 20.51 (Me), 59.10 (C-2), 66.81 (C-1), 111.07 (C-7 Bt), 113.06, 116.12, 118.96 (C-4 Bt), 123.89 (C-5 Bt), 126.99, 127.88, 128.02, 128.06, 128.62 (C-6 Bt), 128.79, 133.07 (C-7a Bt), 134.04, 137.16, 140.53, 144.99 (C-3a Bt) and 147.27.

General Procedure for the Preparation of 1-(*Benzotriazol*-1-*yl*)-1,2-*diarylethylenes* **12**.—The appropriate compound **1** (4.00 mmol) in THF (7 cm^3) was added to a stirred solution of Bu^{t}OK (95%; 0.51 g, 4.80 mmol) in THF (20 cm^3) at −10 °C dropwise. After 10 min compound **5** (0.80 g, 4.40 mmol) in THF (6 cm^3) was added dropwise at 0 °C. The mixture was stirred at 25 °C over 18 h, and water (20 cm^3) was added followed by extraction with diethyl ether (3 × 20 cm^3). The combined organic layers were washed with water (3 × 15 cm^3), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was subjected to silica gel column chromatography (eluent: $CHCl_3$–hexanes 1:5) to yield compounds **12** as main fractions.

1-(*Benzotriazol*-1-*yl*)-1,2-*diphenylethylene* **12a** (a) *From* **1a** *and* **5**. Yield 0.63 g (53%), m.p. 153–154 °C (from hexanes) (Found: C, 80.8; H, 5.0; N, 14.1. $C_{20}H_{15}N_3$ requires C, 80.78; H, 5.08, 14.13%); δ_H 6.74 (2 H, d, *J* 7.3, *o*-H Ph), 7.04–7.40 (12 H, m) and 8.13 (1 H, d, *J* 7.1, 4-H Bt); δ_C 110.49 (C-7 Bt), 119.99 (C-4 Bt), 124.22 (C-5 Bt), 125.92, 127.65, 127.70, 128.04 (C-6 Bt), 128.57, 128.89, 129.32, 133.50 (C-7a Bt), 133.60, 136.66 and 145.83 (C-3a Bt).

(b) *From* **8a**. A stirred mixture of compound **8a** (0.78 g, 2.00 mmol) and NaH (97%; 0.15 g, 6.00 mmol) in dry DMF (6 cm^3) was heated at 80 °C for 20 min. Ice cold 10% aqueous NH_4Cl (20 cm^3) was added after which the mixture was extracted with diethyl ether (3 × 20 cm^3). The combined organic extracts were washed with water (2 × 15 cm^3), dried ($MgSO_4$), and evaporated under reduced pressure to yield the product (0.36 g; 60%).

1-(*Benzotriazol*-1-*yl*)-1-(p-*tolyl*)-2-*phenylethylene* **12b**. (a) *From* **1b** *and* **5**. Yield 0.56 g (44%), m.p. 110–112 °C (from hexanes) (Found: C, 80.95; H, 5.4; N, 13.35. $C_{21}H_{17}N_3$ requires C, 81.00; H, 5.50; N, 13.49%); δ_H 2.36 (3 H, s, Me), 6.72 (2 H, d, *J* 7.7, *o*-H Ph), 7.02–7.38 (11 H, m) and 8.13 (1 H, d, *J* 7.7, 4-H Bt); δ_C 21.26 (Me), 110.56 (C-7 Bt), 119.95 (C-4 Bt), 124.18 (C-5 Bt), 125.85, 126.67, 126.70, 127.98, 128.41 (C-6 Bt), 128.52, 129.59, 133.19, 133.53 (C-7a Bt), 133.75, 133.87, 139.52 and 145.82 (C-3a Bt).

(b) *From* **8b**. A mixture of compound **8b** (0.81 g, 2.00 mmol) and NaH (97%; 0.15 g, 6.00 mmol) in dry DMF (6 cm^3) was heated at 80 °C for 20 min. Ice-cold 10% aqueous NH_4Cl (20 cm^3) was added after which the mixture was extracted with diethyl ether (3 × 20 cm^3). The combined organic layers

were washed with water (3 × 15 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was subjected to silica gel column chromatography (eluent: $CHCl_3$–hexanes 1:4) to yield compound **12b** as the first fraction (0.25 g, 40%). Evaporation of the second fraction yielded compound **1b** (0.09 g, 20%), m.p. 108–109 °C (from methanol) identical (mixed m.p., TLC, NMR) with authentic sample (lit.,[32] m.p. 107 °C).

1-(*Benzotriazol-1-yl*)-1-(p-*chlorophenyl*)-2-*phenylethylene* **12c**. Yield 0.74 g (56%), m.p. 131–132 °C (hexanes) (Found: C, 72.5; H, 4.2; N, 12.65. $C_{20}H_{14}ClN_3$ requires C, 72.40; H, 4.25; N, 12.66%); δ_H 6.72 (2 H, d, *J* 7.6, *o*-H Ph), 7.00–7.40 (11 H, m) and 8.13 (1 H, d, *J* 7.0, 4-H Bt); δ_C 110.33 (C-7 Bt), 120.10 (C-4 Bt), 124.34 (C-5 Bt), 127.20, 128.02, 128.18, 128.26 (C-6 Bt), 128.59, 128.81, 129.11, 129.42, 132.44, 133.30 (C-7a Bt), 135.21, 135.30 and 145.84 (C-3a Bt).

General Procedure for the Preparation of Diarylalkynes **9** *and* **10** *from Compounds* **6–8**.—A stirred solution of Bu'OK (95%; 0.94 g, 8.00 mmol) and the appropriate compound **6–8** (2.00 mmol) in dry DMF (8 cm^3) was heated at 85 °C for 10 min (for **8a**, **b**) or 40 min (for **6a**, **b** and **7**). The reaction mixture was cooled to 25 °C and ice–water (25 cm^3) was added to it; it was then extracted with diethyl ether (3 × 20 cm^3). The combined organic extracts were washed with water (4 × 20 cm^3), dried ($MgSO_4$), and evaporated under reduced pressure. The crude products were purified by silica gel flash chromatography (eluent: hexanes) to yield the diarylalkynes **8**.

Diphenylacetylene **9a** (a). *From* **6a** *or* **8a**. Yield 0.30 g (84% from **6a**) or 0.29 g (80% from **8a**), m.p. 58–60 °C (from methanol) (lit.,[33] m.p. 60 °C); δ_C 89.37 (C≡C), 123.30, 128.24, 128.33 and 131.61.

(b) *From* **1a** *and* **5** (*a one-pot procedure*). A stirred solution of **1a** (0.84 g, 4.00 mmol), **5** (0.80 g, 4.40 mmol) and Bu'OK (95%; 1.89 g, 16 mmol) in dry DMF (16 cm^3) was heated at 85 °C for 20 min. The work-up was carried out as above to yield **9a** (0.57 g, 80%).

(c) *From* **12a**. A stirred solution of compound **12a** (0.59 g, 2.00 mmol) and Bu'OK (95%; 0.47 g, 4.00 mmol) in dry DMF (4 cm^3) was heated at 85 °C for 10 min. Work-up of the reaction mixture was carried out as above to give **9a** (0.30 g, 83%).

(d) *From* **1a**. A stirred solution of compound **1a** (0.84 g, 4.00 mmol) and Bu'OK (95%; 0.94 g, 8.00 mmol) in dry DMF (8 cm^3) was heated at 85 °C for 40 min. Work-up of the reaction mixture was carried out as above to yield **9a** (0.16 g, 22%).

(p-*Tolyl*)*phenylacetylene* **9b**. Yield 0.30 g, 78% (from **6b**) or 0.06 g, 15% (from **12b**), m.p. 71–72 °C (from methanol) (lit.,[33] m.p. 72.5–73.5 °C); δ_C 21.51 (Me), 88.76 and 89.61 (C≡C), 120.23, 123.52, 128.08, 128.33, 129.13, 131.52, 131.55 and 138.38.

(p-*Chlorophenyl*)*phenylacetylene* **9c**. (a) *From* **1c** *and* **5** (*a one-pot procedure*).—The synthesis of **9c** from **1c** (0.97 g, 4.00 mmol) and **5** (0.80 g, 4.40 mmol) was carried out analogously to the preparation of **9a**, method (b). Yield 0.34 g (40%), m.p. 83–84 °C (from methanol) (lit.,[34] m.p. 83–84 °C); δ_C 88.23 and 90.31 (C≡C), 121.77, 122.91, 128.46, 128.53, 128.67, 131.58, 132.79 and 134.23.

(b) *From* **12c**. The synthesis of **9c** from **12c** (0.66 g, 2.00 mmol) and Bu'OK was carried out analogously to the preparation of **9a**, method (c). Yield 0.30 g (70%).

(3-*Thienyl*)*phenylacetylene* **10**. (a) *From* **7**. Yield 0.28 g (75%), m.p. 52–54 °C (from methanol) (Found: C, 78.25; H, 4.35. $C_{12}H_8S$ requires C, 78.22; H, 4.38%); δ_H 7.18 (1 H, d, *J* 3.6, 4-H thien.), 7.23–7.34 (4 H, m) and 7.47–7.53 (3 H, m); δ_C 84.51 and 88.86 (C≡C), 122.24, 123.15, 125.32, 128.15, 128.29, 128.55, 129.81 and 131.47.

(b) *From* **1a** *and* **4** (*a one-pot procedure*). The reaction mixture obtained from **1a** (0.84 g, 4.00 mmol), compound **4** (1.17 g, 4.40 mmol) and LDA as described above for the preparation of **7** was evaporated under reduced pressure (60 °C/1 Torr). The residue was dissolved in dry DMF (16 cm^3) containing Bu'OK (95%, 1.89 g, 16 mmol), and the stirred mixture was heated at 85 °C for 40 min. Work-up of the reaction mixture was carried out analogously to the preparation of **10** from **7** to yield **10** (0.44 g, 60%).

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