The Chemistry of *N*-Substituted Benzotriazoles. Part 6.[1] A New Synthetic Route to Aromatic Ketones

Alan R. Katritzky* and Wojciech Kuzmierkiewicz
Department of Chemistry, University of Florida, Gainesville, Florida 32611, USA

Lithiation of *p*-bis(benzotriazol-1-yl)methyltoluene (**4**) gives the carbanion (**5**) which affords substitution products with many electrophiles. Acidic hydrolysis of the lithiation products affords the corresponding aromatic ketones in good yield. The syntheses of simple ketones, of diketones, and of α-hydroxy ketones are described.

Nucleophilic acylation can be achieved both by direct methods (reactions with acylmetal compounds) and by indirect methods which utilize an acyl anion synthon.[2] The convergent syntheses of carbonyl compounds by means of cyclic 1,3-dithianes[3] or of cyanohydrin silyl ethers[4] as acyl synthons has been the subject of considerable recent interest. It is well known that the benzotriazole ring is a good leading group.[5] We have previously described[1] the synthesis of *p*-bis(benzotriazol-1-yl)methyltoluene (**4**) by reaction of benzotriazole with *p*-tolualdehyde and thionyl chloride. Thus, we thought it of interest to examine the nucleophilicity of the corresponding lithio derivative (**5**) with respect to electrophiles and the possibility of hydrolysis of the products as a potential method for the preparation of ketones.

Lithiation of p-*Bis(benzotriazol-1-yl)methyltoluene* (**4**).—The conversion of (**4**) into the corresponding lithio derivative (**5**) was achieved by adding (**4**) to a solution of lithium diisopropylamide (LDA) in THF at −78 °C and warming to 0 °C to give a clear navy-blue solution. The anion solution was cooled again to −78 °C, and electrophiles were added to it under the conditions shown in Table 1; the progress of the reactions were followed by t.l.c. Purification of the products was achieved by column chromatography; in most experiments some starting material (**4**) was recovered.

Reaction of (**5**) *with Alkyl Halides.*—Alkyl halides reacted readily with (**5**) to give the corresponding alkylated compounds (**7d**—**j**). The yields in these reactions were higher for primary halides than for secondary halides and were also dependent on the leaving group. Thus, 1-bromohexane gives product (**7h**) in higher yield (83%) than 1-iodohexane (52%) (Table 1). These derivatives (**7**) formed by alkyl halides are easily hydrolysed to ketones in the presence of hydrochloric or sulphuric acids (Table 2). The disappearance of the starting material (monitored by t.l.c.) was complete after the times shown in Table 2. After the by-product, benzotriazole, had been filtered off the mixture was extracted with chloroform and the extract was washed with water and evaporated to give the crude ketone which was purified by column chromatography or by recrystallization. The hydrolysis proceeded the fastest with compound (**7f**). This compound is hydrolysed to 1-(*p*-tolyl)-pentan-1-one (**10f**) in THF, with an equimolar amount of 10M HCl at 20 °C after 15 min. Using 5M HCl, complete hydrolysis required 3 h.

The hydrolysis of compound (**7i**) with 10M HCl in refluxing methanol and in methanol or THF at 20 °C gave, 1-(*p*-tolyl)-2-phenylethanone (**10i**), and also some 1-(benzotriazol-1-yl)-1-(*p*-tolyl)-2-phenylethylene (**11**). When 1M HCl was used at 20 °C for 24 h the hydrolysis of (**7i**) gave only the ketone (**10i**). The same result was observed with 98% H_2SO_4 after 15 min. Hydrolysis of (**7i**) with toluene-*p*-sulphonic acid, boron trifluoride, or anhydrous hydrogen chloride gave the alkene (**11**) in addition to the ketone (**10i**). That the formation of compound (**11**) is in competition with the hydrolysis and not an intermediate step was shown by the failure of (**11**) to hydrolyse to the ketone (**10i**) even under forcing conditions. We also observed formation of (**11**) during the pyrolysis of compound (**7i**) at 200 °C.

The hydrolysis of (**7j**) with 10M HCl at 20 °C gave 1-(*p*-tolyl)-3-(benzotriazol-1-yl)butan-1-one (**13**) in 80% yield. However, 4′-

Table 1. Reactions of (**5**) with electrophiles

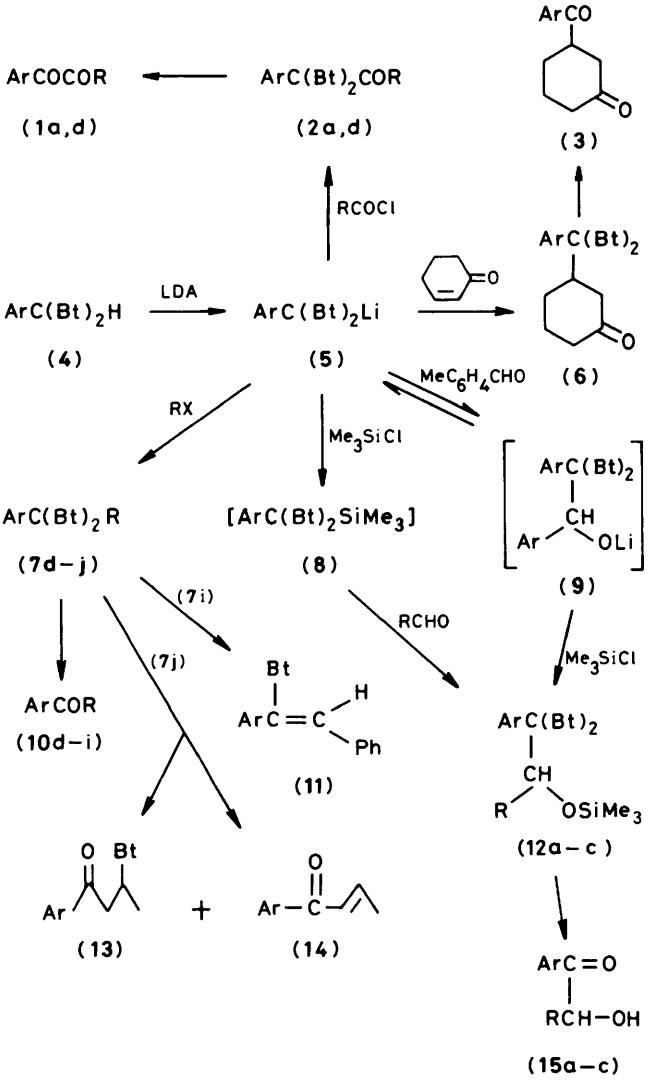
Electrophile	Conditions[a]	Product	Yield (%)	M.p.[b] (°C)	Mol. formula	Required (%) C	H	N	Found (%) C	H	N
MeI	2/1	(**7d**)	92	161—163	$C_{21}H_{18}N_6$	71.16	5.12	23.72	71.0	5.1	23.75
Pr^iI	5/10	(**7e**)	52	205—206	$C_{23}H_{22}N_6$	72.22	5.80	21.98	72.25	5.95	21.95
BuBr	1/6[c]	(**7f**)	78	141—143	$C_{24}H_{24}N_6$	72.70	6.10	21.20	72.65	6.2	21.15
Bu^sBr	7/10	(**7g**)	8	Oil	$C_{24}H_{24}N_6$	72.70	6.10	21.20	72.7	6.1	21.15
HexylI	3/5	(**7h**)	52	95—97	$C_{26}H_{28}N_6$	73.55	6.65	19.80	73.3	6.85	19.6
HexylBr	3/5	(**7h**)	83	95—97	—	—	—	—	—	—	—
$PhCH_2Br$	2/1	(**7i**)	95	158—160[d]	$C_{27}H_{22}N_6$	75.32	5.15	19.53	75.55	5.25	19.35
AllylBr	2/1	(**7j**)	84	161—163	$C_{23}H_{20}N_6$	72.61	5.30	22.09	72.6	5.35	22.15
MeCOCl	6/8	(**2d**)	45	188—190	$C_{22}H_{18}N_6O$	69.09	4.74	21.98	68.85	4.9	21.7
PhCOCl	2/1	(**2a**)	61	247—249[d]	$C_{27}H_{20}N_6O$	72.95	4.54	18.91	72.75	4.55	18.75
Cyclohexenone	2/2	(**6**)	78	270—272[d]	$C_{26}H_{24}N_6O$	71.54	5.54	19.26	71.55	5.45	19.15
$Me_3SiCl/PhCHO$	Method B	(**12a**)	60	177—178	$C_{30}H_{30}N_6OSi$	69.47	5.83	16.20	69.3	5.95	16.0
$p\text{-}MeC_6H_4CHO/Me_3SiCl$	Method A	(**12b**)	68 (76)[e]	187—189	$C_{31}H_{32}N_6OSi$	69.89	6.05	15.78	70.05	6.15	15.7
$Me_3SiCl/PrCHO$	Method B	(**12c**)	6	148—149	$C_{27}H_{32}N_6OSi$	66.90	6.66	17.34	66.8	6.85	17.1

[a] Hours at −78 °C/hours at r.t. [b] Recrystallized from MeOH. [c] At 0° C. [d] Recrystallized from acetone. [e] Method B.

Table 2. Hydrolysis of bisbenzotriazoles to ketones

Compound	Solvent	Acid	Temp.	Time	Yield (%)	Product
(**7d**)	THF	10M HCl	R.t.	10 h	95	(**10d**)
(**7e**)	THF	10M HCl	R.t.	10 h	84	(**10e**)
(**7f**)	THF	5M HCl	R.t.	3 h	95	(**10f**)
(**7g**)	THF	10M HCl	R.t.	10 h	91	(**10g**)
(**7h**)	THF	10M HCl	R.t.	20 h	96	(**10h**)
	THF	10M HCl	Reflux	2 h	96	(**10h**)
(**7i**)	Me_2CO	10M HCl	R.t.	1 h	49 [a]	(**10i**)
	THF	1M HCl	R.t.	24 h	92	(**10i**)
	THF	98% H_2SO_4	R.t.	15 min	93	(**10i**)
(**7j**)	THF	10M HCl	R.t.	12 h	80	(**13**)
	THF	98% H_2SO_4	R.t.	3 h	75 [b]	(**14**)
(**2d**)	THF	10M HCl	R.t.	10 h	92	(**1d**)
(**2a**)	THF	10M HCl	R.t.	5 h	88	(**1a**)
(**6**)	Me_2CO	10M HCl	Reflux	1.5 h	85	(**3**)
	THF	10M HCl	R.t.	24 h	92	(**3**)
(**12a**)	THF	10M HCl	R.t.	24 h	95	(**15a**)
(**12b**)	THF	10M HCl	R.t.	24 h	95	(**15b**)
(**12c**)	THF	10M HCl	R.t.	2 h	91	(**15c**)

[a] Formation of (**11**) was observed (see Experimental section). [b] Formation of (**13**) was also observed.



Bt = Benzotriazol-1-yl. Ar = *p*-Tolyl. R: **a** = Ph, **b** = *p*-MeC_6H_4, **c** = Pr, **d** = Me, **e** = Pr^i, **f** = Bu, **g** = Bu^s, **h** = hexane, **i** = CH_2Ph, **j** = allyl.

methylcrotonophenone (**14**) was the major product (75%) when (**7j**) was hydrolysed with 98% H_2SO_4 in THF. Compound (**13**) was evidently formed by Michael addition of the benzotriazole, present in solution during the hydrolysis, to the isomerized ketone (**14**).

Reaction of (**5**) *with Acid Chlorides.*—Acylation of (**5**) with benzoyl chloride and acetyl chloride afforded the corresponding products (**2a**) (45%) and (**2d**) (61%) (Table 1). The reaction of ethyl benzoate with (**5**) did not give (**2a**); instead the starting material was recovered. Hydrolysis of (**2d**) and (**2a**) with 10M HCl gave 1-(*p*-tolyl)propane-1,2-dione (**1d**) and p-methylbenzil (**1a**), respectively in good yields (Table 2).

Reaction of (**5**) *with Cyclohex-2-en-1-one.*—The Michael addition of (**5**) to cyclohex-2-en-1-one gave bis(benzotriazol-1-yl)-(3-oxocyclohexyl)-*p*-tolylmethane (**6**) in 78% yield (Table 1). However, attempted reaction with 4-vinylpyridine, chalcone, ethyl acrylate, and acrylonitrile gave only recovered starting material (**5**). The hydrolysis of (**6**) with 10M HCl gave 3-(*p*-toluoyl)cyclohexanone (**3**) in good yield (Table 2). Treatment of compound (**6**) with sodium ethoxide in boiling ethanol for 15 min yielded compound (**4**) and cyclohex-2-en-1-one.

Formation of Hydroxy Ketones (**15a**—**c**).—An attempted reaction of (**5**) with *p*-tolualdehyde resulted in recovery of the starting material. The same result was obtained in the presence of TMEDA or HMPT. However, when trimethylsilyl chloride was added to the reaction mixture, the silyl ether (**12b**) was isolated in 60% yield. This suggests that the adduct (**9**) is present in small amount in equilibrium with (**5**). Alternatively, compound (**5**) can be trapped with trimethylsilyl chloride to give (**8**); this hydrolyses quickly when its isolation is attempted but reacts with *p*-tolualdehyde in dry DMF in the presence of caesium fluoride[6] to give (**12**) in 76% yield. Similarly, compound (**8**) reacted with benzaldehyde and with butyraldehyde (6% yield) under the same conditions to give the expected products (Table 1). However, ketones failed to react with (**8**). The hydrolyses of (**12a**), (**12b**), and (**12c**) gave the corresponding hydroxy ketones (**15a**), (**15b**), and (**15c**) respectively.

The lack of reactivity of the carbanion (**5**) towards ketones and aldehydes can be explained in terms of steric factors. The literature shows that compounds of the triarylmethyl type (**5**) react sluggishly with electrophiles.[2c]

Table 3. Spectral data for the derivatives of (**5**)

Compound	I.r. ($\nu_{max.}$/cm^{-1}) ($CHBr_3$)	^{1}H N.m.r. (δ, *J* in Hz; $CDCl_3$) $PhCH_3$	Aromatic	R
(**7d**)	1 610, 1 585 (N=N), 1 450, 1 385, 920, 783, 740	2.42 (3 H, s)	6.57—7.53 (10 H, m) 8.05—8.28 (2 H, m)	3.43 (3 H, s)
(**7e**)	1 610, 1 588 (N=N), 1 490, 1 450, 1 370 (broad), 1 070 (broad), 1 000	2.40 (3 H, s)	7.06–7.42 (10 H, m) 7.88—8.18 (2 H, d)	1.05 (6 H, d, *J* 6) 4.91 (1 H, m)
(**7f**)	2 960, 2870 (CH aliph), 1 610, 1 590 (N=N), 1 490, 1 450, 1 285, 1 020	2.40 (3 H, s)	6.97—7.50 (10 H, m) 7.97—8.24 (2 H, m)	0.85 (3 H, t), 1.15—1.50 (4 H, m), 3.61 (2 H, m)
(**7g**)	2 955, 2 880, (CH aliph), 1 610, 1 585 (N=N), 1 485, 1 450, 1 275, 930	2.44 (3 H, s)	7.05—7.30 (10 H, m) 7.90—8.05 (2 H, d)	0.95—1.15 (6 H, m), 1.75—1.90 (2 H, m), 4.55 (1 H, m)
(**7h**)	2 950, 2 920 (Ch aliph), 1 605, 1 585 (N=N), 1 350, 1 280(br)	2.40 (3 H, s)	6.85—7.50 (10 H, m) 7.92—8.30 (2 H, m)	0.88 (3 H, t), 1.31 (8 H, m) 3.63 (2 H, m)
(**7i**)	1 610, 1 590 (N=N), 1 450, 1 285, 960, 780, 745	2.33 (3 H, s)	6.50—7.50 (15 H, m) 8.00—8.26 (2 H, m)	5.03 (2 H, s) phenyl protons, see aromatic region
(**7j**)	2 920, 1 640 (C=C), 1 610, 1 590 (N=N), 1 490, 1 450, 1 287, 1 000	2.40 (3 H, s)	6.85—7.47 (10 H, m) 8.00—8.12 (2 H, d, J_6)	4.40 (2 H, d, *J*6) 4.90—5.05 (2 H, m) 5.80—6.00 (1 H, m)
(**2d**)	1 735 (C=O), 1 610, 1 590 (N=N) 1 290, 1 010, 940, 745	2.41 (3 H, s)	6.95—7.65 (10 H, m) 7.90—8.15 (2 H, m)	2.31 (3 H, s)
(**2a**)	2 960, 2 920 (CH aliph), 1 610, 1 590 (N=N), 1 250, 1 100 (O–Si), 1 250 (SiMe)	2.37 (3 H, s)	6.66—7.50 (15 H, m) 8.03—8.33 (2 H, m)	0.2 (9 H, s), 2.27 (3 H, s)
(**6**)	1 710 (C=O), 1 605, 1 585 (N=N) 1 005, 940, 750	2.40 (3 H, s)	6.72—7.36 (10 H, m) 7.85—8.24 (2 H, m)	0.90—2.37 (8 H, m)
(**12a**)	2 960, 2 920 (CH aliph), 1 610, 1 590 (N=N), 1 250 (O–Si), 1 100 (O–Si), 840	2.41 (3 H, s)	6.70—7.41 (15 H, m) 8.07—8.18 (2 H, m)	0.2 (9 H, s) phenyl protons, see aromatic region
(**12b**)	2 960, 2 920 (CH aliph), 1 610, 1 585 (N=N), 1 250 (Si–Me), 1 100 (Si–O)	2.37 (3 H, s)	6.66—7.50 (15 H, m) 8.03—8.33 (2 H, m)	0.2 (9 H, s) 2.27 (3 H, s)
(**12c**)	2 950, 2 960, (CH aliph), 1 610, 1 590 (N=N), 1 450, 1 250 ($SiCH_3$), 1 105 (O–Si)	2.40 (3 H, s)	6.65—7.35 (10 H, m) 7.95—8.06 (2 H, m)	0.2 (9 H, s) 0.95 (3 H, t, *J* 6) 1.04—1.70 (2 H, m) 1.92—2.12 (2 H, m) 6.03—6.15 (1 H, t, *J* 6)

Table 4. Analytical data of ketones

Compound	M.p. (°C)	Lit. m.p. (°C)	Formula	Required (%) C	H	N	Found (%) C	H	N
(**10d**)	Oil		$C_9H_{10}O$	80.56	7.51		80.43	7.53	
(**10e**)	Oil		$C_{11}H_{14}O$	81.44	8.70		81.28	8.74	
(**10f**)	20	20[a]	$C_{12}H_{16}O$	81.77	9.15		81.75	9.10	
(**10g**)	Oil		$C_{12}H_{16}O$	81.77	9.15		81.65	9.21	
(**10h**)	42—42.5		$C_{14}H_{20}O$	82.30	9.87		82.58	9.58	
(**10i**)	108—110	108—110[b]	$C_{15}H_{14}O$	85.68	6.71		85.85	6.93	
(**13**)	Oil		$C_{17}H_{16}N_3O$	73.36	5.79	15.10	73.15	5.68	15.21
(**14**)	Oil		$C_{11}H_{12}O$	82.46	7.55		82.37	7.71	
(**1d**)	Oil		$C_{10}H_{10}O_2$	74.08	6.17		74.24	6.05	
(**1a**)	29—30	31[c]	$C_{15}H_{12}O_2$	80.33	5.40		80.17	5.62	
(**3**)	71—73		$C_{14}H_{16}O_2$	77.74	7.46		77.50	7.55	
(**15a**)	97—98	99[d]	$C_{15}H_{14}O_2$	79.62	6.24		79.42	6.50	
(**15b**)	85—87	87—88[e]	$C_{16}H_{16}O_2$	79.97	6.71		79.61	6.95	
(**15c**)	Oil		$C_{12}H_{16}O_2$	74.96	8.39		74.85	8.51	

[a] P. J. Wagner, M. J. Thomas, and E. Harris, *J. Am. Chem. Soc.*, 1976, **98**, 7675. [b] M. S. Newman and R. Gaertner, *J. Am. Chem. Soc.*, 1950, **72**, 264. [c] H. H. Halt, A. Pilgrim, and W. J. Hurran, *J. Chem. Soc.*, 1936, 93. [d] A. Weissberger, E. Strasser, H. Mainz, and W. Schwarze, *Justus Liebigs Ann. Chem.*, 1930, **478**, 112. [e] H. Suzuki, *Bull. Chem. Soc. Jpn.*, 1960, **33**, 406.

All the compounds prepared were characterized spectrally. Spectral data for the derivatives of (**5**) and for ketones are given in Tables 3 and 5. The benzotriazoles described are all 1-substituted as shown by two absorptions at *ca.* 1 585—1 580 and 1 605—1 610 cm^{-1} in their i.r. spectra. Their ^{1}H n.m.r. spectra in $CDCl_3$ display one of the benzotriazole ring protons characteristically deshielded at 7.85—8.33 p.p.m.

Conclusions

When our benzotriazole system is compared with other acyl anion equivalents such as dithianes[3] and cyanohydrin silyl ethers[4] it is apparent that the methods are similar in terms of yields but our conditions of hydrolysis are milder. However, we are limited to aryl alkyl ketones since the lithiation of alkylbisbenzotriazoles was unsuccessful.[5] All the derivatives of

Table 5. Spectral data of ketones

Compound	I.r. (ν C=O/cm^{-1}) ($CHBr_3$ or film)	^{1}H n.m.r. (δ, *J* in Hz; $CDCl_3$) ArCH_3	Aromatic	R
(**10d**)	1 680	2.39 (3 H, s)	7.33 (2 H, d, *J* 8) 7.97 (2 H, d, *J* 8)	2.51 (3 H, s)
(**10e**)	1 685	2.40 (3 H, s)	7.20 (2 H, d, *J* 8) 7.86 (2 H, d, *J* 8)	1.20 (6 H, d, *J* 7) 2.50 (1 H, m)
(**10f**)	1 680	2.39 (3 H, s)	7.30 (2 H, d, *J* 8) 7.97 (2 H, d, *J* 8)	0.90 (3 H, t), 1.58 (4 H, m), 2.94 (2 H, t, *J* 7)
(**10g**)	1 675	2.40 (3 H, s)	7.33 (2 H, d, *J* 8) 7.88 (2 H, d, *J* 8)	1.05—1.52 (6 H, m) 1.95 (2 H, m), 2.85 (1 H, m)
(**10h**)	1 680	2.42 (3 H, s)	7.33 (2 H, d, *J* 8) 7.98 (2 H, d, *J* 8)	0.91 (3 H, t), 1.06—2.00 (8 H, m), 2.97 (2 H, t, *J* 6)
(**10i**)	1 680	2.42 (3 H, s)	7.18—7.50 (7 H, m) 8.03 (2 H, d, *J* 8)	4.30 (2 H, s)
(**13**)	1 685	2.38 (3 H, s)	7.20 (2 H, d, *J* 8) 7.30—7.75 (3 H, m) 7.84 (2 H, d, *J* 8) 8.05 (1 H, d, *J* 8)	1.86 (3 H, d, *J* 7) 3.60—4.14 (2 H, dd) 5.60 (1 H, m)
(**14**)	1 675	2.41 (3 H, s)	7.28 (2 H, d, *J* 8) 7.85 (2 H, d, *J* 8)	2.00 (3 H, d, *J* 7) 6.54—7.18 (2 H, m)
(**1d**)	1 630, 1 705	2.36 (3 H, s)	7.28 (2 H, d, *J* 8) 7.82 (2 H, d, *J* 8)	2.15 (3 H, s)
(**1a**)	1 630, 1 685	2.40 (3 H, s)	7.30—7.72 (5 H, m) 7.90—8.24 (4 H, m)	See aromatic region
(**3**)	1 680, 1 710	2.40 (3 H, s)	7.28 (2 H, d, *J* 8) 7.94 (2 H, d, *J* 8)	1.30—2.55 (11 H, m) 3.85 (1 H, m)
(**15a**)	1 675	2.35 (3 H, s)	7.18 (2 H, d, *J* 9) 7.23—7.40 (5 H, m) 7.82 (2 H, d, *J* 9)	4.58 (1 H, d, *J* 6) 5.92 (1 H, d, *J* 6)
(**15b**)	1 675	2.37 (3 H, s)	6.96—7.36 (6 H, m) 7.85 (2 H, d, *J* 8) 5.97 (1 H, d)	2.30 (3 H, s) 4.59 (1 H, d, *J* 6)
(**15c**)	1 680	2.38 (3 H, s)	7.20 (2 H, d, *J* 8) and 7.90 (2 H, d, *J* 8)	0.96 (3 H, t, *J* 6) 1.1—1.85 (4 H, m) 4.35 (1 H, br s) 5.95 (1 H, s)

(**5**) were hydrolysed to ketones in THF in the presence of equimolar amounts of hydrochloric acid at room temperature. We found that hydrolysis in refluxing THF is faster and does not cause decomposition.

Experimental

General experimental procedures are given in the preceding paper.[1] Solvents and all reagents were carefully dried, tetrahydrofuran (THF) was refluxed over and distilled from sodium–benzophenone ketyl immediately prior to use, di-isopropylamine was refluxed overnight and distilled from calcium hydride. The molarity of BuLi was checked regularly by titration.[7] Reagents were routinely distilled and stored over 4Å molecular sieves. The reactions were followed by t.l.c.

General Procedure for the Lithiation of (**5**) *and subsequent Reaction with Electrophiles.*—To a stirred solution of di-isopropylamine (1.1 g, 11 mmol) in THF (20 ml) was added BuLi (2.5 M in hexane; 4 ml, 10 mmol) at −15 °C by syringe under argon. The mixture was stirred for 15 min at −15 °C and 30 min at 0 °C and then cooled to −78 °C. Then a solution of (**4**) (3.4 g, 10 mmol) in THF (30 ml) was added. This gave a navy-blue solution of the anion (**5**) immediately. The reaction mixture was kept at −78 °C for 1 h, and at room temperature for a further 1 h. A solution of the electrophile (10 mmol) in THF (10 ml was added and the reaction carried out under the conditons shown in Table 1.) Saturated aqueous NH_4Cl (50%, v/v) was then added. The organic layer was separated, and the aqueous layer was extracted with ether (3 × 10 ml). The combined organic layers was washed with water (10 ml) and dried ($MgSO_4$). The solvent was evaporated and the residue was recrystallized [compounds (**10d, i, j**)] or subject to column chromatography [silica gel (230—400 mesh), hexane–$CHCl_3$ (2:1)] and then recrystallized. Analytical and spectral data are given in Tables 1 and 4.

Preparation of Compounds (**12a—c**).—*Method A.* To a solution of compound (**5**) (10 mmol) (prepared as described above) was added *p*-tolualdehyde (1.2 g, 10 mmol) in THF (5 ml) at −78 °C over 1 h; trimethylsilyl chloride (1.08 g, 10 mmol) in THF (4 ml) was then added and the mixture stirred for 8 h at −78 °C and at room temperature for a further 8 h. The product was isolated using the general procedure described above. After separation by column chromatography [hexane–$CHCl_3$ (1:1)], compound (**12b**) was recrystallized.

Method B. A solution of trimethylsilyl chloride (2.16 g, 20 mmol) in THF (5 ml) was added dropwise to a solution of compound (**5**) (10 mmol) in THF (30 ml) at −78 °C under argon. The reaction mixture was stirred for 5 h at −78 °C and at room temperature for a further 5 h; the THF was then evaporated off. Dry DMF (10 ml), the aldehyde (10 mmol), and caesium fluoride (1.52 g, 10 mmol; dried before use at 100 °C *in vacuo*) were added and the resulting mixture was stirred at room temperature under argon for 20 h. Water (10 ml) was added and the mixture extracted with $CHCl_3$ (3 × 10 ml). The combined organic extracts was dried ($MgSO_4$) and evaporated and the oily residue was separated by column chromatography

[benzene–ethyl acetate (3:1)]. Analytical and spectral data for (**12a**—**c**) are given in Tables 1 and 4.

General Procedure for the Hydrolysis of Compounds (**2**), (**6**), (**7**), and (**12**).—To a stirred solution of the bisbenzotriazolyl derivative (1 mmol) in the appropriate solvent (10 ml) was added the acid (1 mmol) at 25 °C (Table 2). The reaction mixture was stirred for the appropriate time. After hydrolysis was complete the protonated benzotriazole was filtered off, the solvent was evaporated, and the residue was partitioned between water (5 ml) and $CHCl_3$ (3 × 5 ml). The combined organic extracts were washed with water (5 ml), dried ($MgSO_4$), and evaporated and the resulting crude material was purified by crystallization or column chromatography [benzene–ethyl acetate (5:1)]. Specific reaction conditions and analytical and spectral data are given in Tables 2, 5, and 6.

Preparation of 1-(*Benzotriazol*-1-*yl*)-1-(p-*tolyl*)-2-*phenylethylene* (**11**).—Bis(benzotriazol-1-yl)(benzyl)-*p*-tolylmethane (**7i**) (1 g, 2.3 mmol) was heated at 200 °C for 0.5 h. After being cooled the reaction mixture was purified by column chromatography [hexane–$CHCl_3$ (2:1)]. The first fraction was shown to be (**7i**) (0.43 g, 50%), m.p. 102–103 °C (Found: C, 81.4; H, 5.5; N, 13.4. $C_{21}H_{17}N_3$ requires C, 81.0; H, 5.50; N, 13.50%); $\nu_{max.}$($CHBr_3$) 2 950, 1 630, 1 610, 1 446, 1 350, and 1 060; δ_H (60 MHz; $CDCl_3$) 8.30—8.06 (1 H, m), 7.47—6.75 (13 H, m), and 2.39 (3 H, s); *m*/*z* 311 (M^+, 17%), 284 (14), 283 (70), 282 (100), 281 (29), 268 (43), 267 (50), 193 (20), 178 (35), 166 (20), 165 (88), 152 (14), 133 (22), 118 (8), 115 (20), and 91 (11). The second fraction, a white crystalline solid, was characterized as benzotriazole (0.16 g, 29%). Compound (**11**) was also obtained when (**7f**) was hydrolysed with 10M HCl (Table 2).

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