

The Chemistry of *N*-Substituted Benzotriazoles. Part 5.¹ Reactions of Benzotriazole with Aldehydes and Thionyl Chloride—Formation of (Benzotriazol-1-yl)-1-chloroalkanes and Bis(benzotriazolyl)alkanes

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Reaction of benzotriazole with an excess of aliphatic aldehydes and thionyl chloride in refluxing chloroform gives the corresponding 1-(benzotriazol-1-yl)-1-chloroalkanes. Products with an α -hydrogen next to the chlorine-bearing carbon atom gradually eliminate hydrogen chloride with time or when heated. Nucleophilic displacements of the chlorine atom are described. Reaction of 2 mol equiv. of benzotriazole with 1 mol equiv. of aromatic or aliphatic aldehydes and an excess of thionyl chloride yields the corresponding bis(benzotriazol-1-yl)methylarenes and 1,1-bis(benzotriazol-1-yl)alkanes respectively; usually some of the corresponding 1-(benzotriazol-1-yl)-1-(benzotriazol-2-yl)alkanes are also formed. The 1-(benzotriazol-1-yl)-1-chloro-1-arylmethanes spontaneously react further to give bisbenzotriazolyl compounds.

Continuing with our studies of the synthetic use of *N*-substituted benzotriazoles we report here the reaction of benzotriazole with aldehydes and thionyl chloride to give either the 1-(benzotriazol-1-yl)-1-chloroalkanes, (2) and (7), or the bisbenzotriazolyl compounds, (5) and (8), depending upon the reaction conditions employed. These compounds are of considerable synthetic interest.²

Investigations³ of 1-chloromethylbenzotriazole⁴ have demonstrated that benzotriazole effectively stabilises an *N*-chloromethyl group due to the electron-withdrawing ability of the triazole ring, as reflected by the high acidity (pK_a 8.2)⁵ of benzotriazole. The *N*-chloromethyl derivatives of benzimidazole (pK_a 13.2)⁶ and pyrazole (pK_a 14.2)⁷ are stable only when protonated.⁸⁻¹⁰

1-Chloromethylbenzotriazole undergoes substitution by carbon, nitrogen, phosphorus and sulphur nucleophiles.³ α -Lithiation of 1-phenylthiomethylbenzotriazole occurs readily.³ 1-(α -Hydroxyalkyl)benzotriazoles are formed on reaction of benzotriazole with aldehydes,¹¹ and further reaction with alcohols yields 1-(α -alkoxyalkyl) benzotriazoles.¹¹ Reaction of 1-(α -hydroxyalkyl)benzotriazoles with aromatic and heteroaromatic primary amines yields mono-*N*-[1-(benzotriazol-1-yl)alkyl] derivatives,¹² which are converted upon reduction into mono *N*-alkylated aromatic and heteroaromatic amines¹ and upon treatment with Grignard reagents into *N*-(secondary alkyl)arylamines.¹

Chloroalkylation of Benzotriazole.—The reaction of benzotriazole with formaldehyde to give 1-hydroxymethylbenzotriazole and its transformation to 1-chloromethylbenzotriazole on treatment with thionyl chloride is well known.⁴ We,¹¹ and others,¹³⁻¹⁵ have generalised the first step of this sequence: aldehydes with benzotriazole give 1-hydroxyalkylbenzotriazoles. We expected that treatment of these compounds *in situ* with thionyl chloride should yield the corresponding 1-chloroalkylbenzotriazoles. The few previously known 1-(*N*-azolyl)-1-chloroalkanes were generally prepared by addition of hydrogen chloride to the corresponding alkene.^{16,17} However, 1-pyrazol-1(2-yl)-1-chloroalkane hydrochlorides have been reported in the patent literature from reactions of pyrazole with aldehydes and thionyl chloride.¹⁸

We find that refluxing benzotriazole with an excess of an aliphatic aldehyde and thionyl chloride in chloroform for 30 min gives good yields of the corresponding 1-(benzotriazol-1-

yl)-1-chloroalkanes (2a-f) (Scheme and Table 1). The stability of compounds (2a-d,f) is somewhat limited, due to the hydrogen α to the chlorine-bearing carbon atom. Compounds (2a-c,f) with a primary alkyl chain eliminate hydrogen chloride more rapidly, whereas (2d; R = Prⁱ) with a secondary alkyl chain is stable at 20 °C once isolated, although elimination to the alkene [6a; R' = Me] occurred during preparation. Compound (2e) with a *t*-alkyl group is quite stable. 1-(Benzotriazol-1-yl)-1-chloroalkanes (2) with nucleophiles yield the corresponding substituted derivatives (3) (Scheme) as expected. Reaction of benzotriazole with aromatic aldehydes always leads to the bisbenzotriazole compounds, even when an excess of aldehyde with respect to benzotriazole is used.

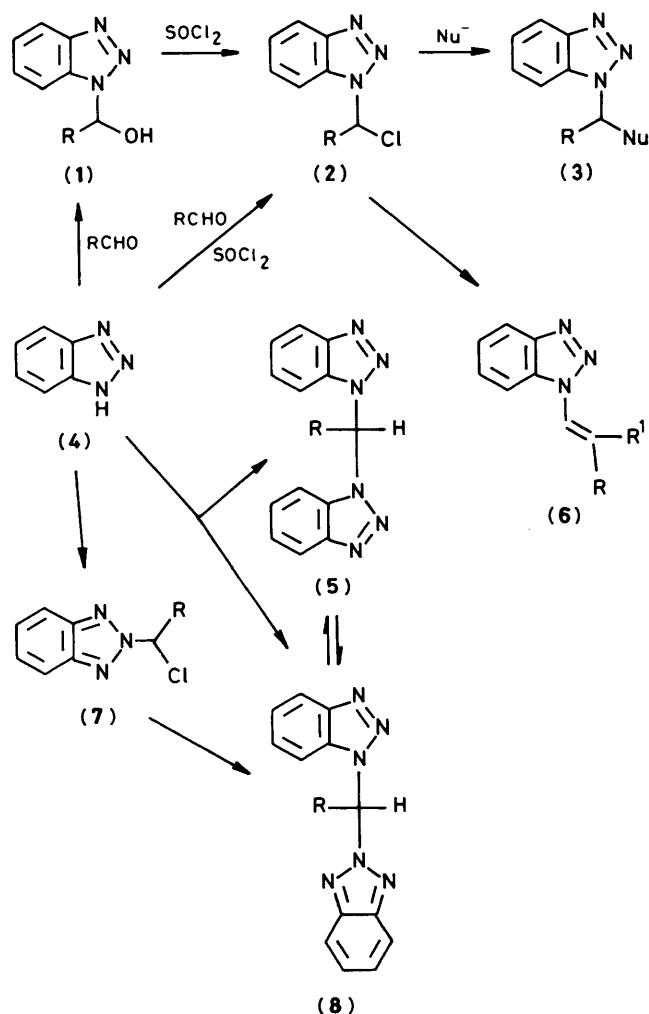
Spectroscopic data (Tables 3 and 4 and the Experimental section) fully support structures (2a-f). The corresponding 1-(benzotriazol-2-yl)-1-chloroalkanes (7) were not isolated from these reactions although trace amounts were detected in some crude reaction products by t.l.c. and n.m.r. analysis. Compounds of type (7) have, however, been isolated as minor by-products in the preparation of bisbenzotriazolylalkanes (see below).

Bis(benzotriazolyl)alkanes.—Bis(benzotriazol-1-yl)methane and (benzotriazol-1-yl)(benzotriazol-2-yl)methane were first prepared in 1952 from the reaction of 1-(chloromethyl)benzotriazole with benzotriazole and sodamide.⁴ Bis(benzotriazol-1-yl)methane was also isolated as a side product in the reaction of 1-hydroxymethylbenzotriazole with benzoyl chloride.^{19a} Benzotriazolyl(diphenyl)methyl chloride (formed by reaction of benzophenone hydrazone with 1-chlorobenzotriazole reacts with further 1-chlorobenzotriazole to give bis(benzotriazol-1-yl)(diphenyl)methane.^{19b} Reaction of pyrazole with acetals and ketals in the presence of toluene-*p*-sulphonic acid yields bispyrazolylalkanes.²⁰ Recently, bisazol-*N*-ylmethanes have received more attention: Elguero *et al.*²¹ prepared several bisazol-*N*-ylmethanes including derivatives of benzotriazole, pyrazole, 1,2,4-triazole, benzimidazole, and indazole by reaction of the azole with dichloromethane under phase-transfer conditions. The only other report of bis(benzotriazolyl)alkanes appears to be a Russian claim²² to have isolated 1,1-bis(benzotriazol-1-yl)ethane. A few reactions of bisazolylalkanes have been studied: *e.g.* the quaternization of 1,1'-methylenediimidazole and 1,1'-methylenedibenzimidazole,^{21c} and the lithiation²³ of gem-bis(pyrazol-1-yl)alkanes.

Table 1. 1-(Benzotriazol-1-yl)-1-chloroalkanes (2)

Compd. no.	R	Molecular formula	Yield (%)	M.p. (°C)	Found (%) (Required)		
					C	H	N
(2a)	Me	C ₈ H ₈ ClN ₃	55	Oil	52.8 (52.90)	4.4 (4.44)	23.05 (23.14)
(2b)	Et	C ₉ H ₁₀ ClN ₃	52	Oil	54.85 (55.25)	5.2 (5.15)	21.5 (21.48)
(2c)	Pr	C ₁₀ H ₁₂ ClN ₃	100	Oil ^a	—	—	—
(2d)	Pr ⁱ	C ₁₀ H ₁₂ ClN ₃	51	60–63 ^b	57.5 (57.28)	6.05 (5.73)	20.2 (20.05)
(2e)	Bu ⁱ	C ₁₁ H ₁₄ ClN ₃	82	93–95 ^c	59.3 (59.06)	6.65 (6.26)	18.9 (18.79)
(2f)	Oct ⁿ	C ₁₅ H ₁₈ ClN ₃	98	Oil	64.3 (64.39)	8.05 (7.93)	15.15 (15.02)

^a B.p. 120 °C/2 mmHg; decomposes slowly at 20 °C. ^b From pentane. ^c From hexane.



Scheme. R: a = Me, b = Et, c = Pr, d = Prⁱ, e = Buⁱ, f = Oct, g = Ph, h = *p*-MeC₆H₄, i = Hep

We find that the reaction of 2 mol equiv. of benzotriazole with 7 mol equiv. of an aliphatic or aromatic aldehyde and an excess of thionyl chloride yields a mixture of the 1,1-bis(benzotriazol-1-yl)alkanes (5) and 1-(benzotriazol-1-yl)-1-(benzotriazol-2-yl)alkanes (8) or bis(benzotriazol-1-yl)methylarenes (5) and (benzotriazol-1-yl)(benzotriazol-2-yl)methylarenes (8) which

can be separated by chromatography. The 1,1-adduct (5) is always the major product, and in the case of aromatic aldehydes the yield of the 1,2-adduct (8) is very small (Table 2). The reaction is much slower if an inert solvent is employed and incomplete reaction occurs unless an extended period of reflux is used. Traces of the corresponding 1-(benzotriazol-2-yl)- (7) and 1-(benzotriazol-1-yl)-1-chloroalkane (2) are frequently isolated as by-products in the case of aliphatic aldehydes (but absent in the cases of aromatic aldehydes), and if the structure of (2) is such that it readily eliminates hydrogen chloride (see above) a trace of alkene (6) is generally also present (see Experimental section for details).

The 1,1- and 1,2-adducts (5) and (8) are readily distinguished by spectroscopic methods and by differences in melting point. The 1,1-adducts have the higher melting point and are more polar, and are thus eluted later from the chromatography column than their 1,2-analogues.

Interconversion was attempted by refluxing the pure 1,1- (5) and 1,2-adducts (8), separately in thionyl chloride. T.l.c. analysis revealed that the equilibration between the two isomers is very slow; even after refluxing for 5 days only traces of the other isomer (8) or (5) could be detected, together with some of the corresponding chloro compounds (2) or (7).

Distinguishing Spectral Features of Compounds (2) from (7) and (5) from (8).—The 1-(benzotriazol-1-yl)-1-chloroalkanes (2) and 1-(benzotriazol-2-yl)-1-chloroalkanes (7) can be readily distinguished^{24,25} by their ¹H and ¹³C n.m.r. spectra [see Tables 3 and 4 for compounds (2) and Experimental section for compounds (7)]. The ¹H spectra of (2) show an ABCD pattern in the aromatic region whereas compounds (7) show a symmetrical AA'BB' pattern characteristic of the isobenzotriazole system, *cf.* 1- and 2-methylbenzotriazoles.²⁴ The chemical shifts of the alkyl protons in the *N*-substituent also differ very slightly. The ¹³C n.m.r. spectra of compounds (2) (see Table 4) show six aromatic carbon signals whereas compounds (7) show only three signals, as expected.²⁵

Differentiation between the 1,1-(bisbenzotriazol-1-yl)alkanes (5) and 1-(benzotriazol-1-yl)-1-(benzotriazol-2-yl)alkanes (8) by ¹H n.m.r. spectroscopy is difficult since the methine proton also absorbs in the aromatic region. However, the ¹³C n.m.r. spectra are quite clear cut: the 1,1-compounds (5) show only six aromatic carbons whereas the 1,2-compounds (8) exhibit nine aromatic signals (Table 6). The chemical shift of the methine carbon is further downfield for the 1,2-adduct (8). Slight differences in the chemical shift values of the alkyl protons are also observed in the ¹H n.m.r. spectra (Table 5). The ¹³C and ¹H n.m.r. spectra of these compounds (5) and (8) agree with those

Table 2. Bisbenzotriazoles (5) and (8)

Compd. no.	R	Formula	Yield (%)	Recryst. Solv.	M.p. (°C)	Found (%) (Required)		
						C	H	N
(5a)	Me	C ₁₄ H ₁₂ N ₆	32	MeOH	141—142 ^a	63.47 (63.62)	4.52 (4.58)	32.03 (31.80)
(8a)	Me	C ₁₄ H ₁₂ N ₆	5	Oil		63.51 (63.62)	4.62 (4.58)	31.77 (31.80)
(5b)	Et	C ₁₅ H ₁₄ N ₆	60	MeOH	128—129	65.03 (64.73)	5.17 (5.07)	30.40 (30.20)
(8b)	Et	C ₁₅ H ₁₄ N ₆	13	MeOH	98—99	64.40 (64.73)	5.08 (5.07)	30.07 (30.20)
(5c)	Pr	C ₁₆ H ₁₆ N ₆	29	Pentane-ether	107—108	65.63 (65.73)	5.67 (5.52)	28.76 (28.75)
(8c)	Pr	C ₁₆ H ₁₆ N ₆	14	Oil		65.69 (65.73)	5.58 (5.52)	28.59 (28.75)
(5d)	Pr ⁱ	C ₁₆ H ₁₆ N ₆	41	EtOH	147—149	65.34 (65.75)	5.54 (5.48)	28.59 (28.77)
(8d)	Pr ⁱ	C ₁₆ H ₁₆ N ₆	18	EtOH	135—136	65.52 (65.75)	5.58 (5.48)	28.62 (28.77)
(5e)	Bu ⁱ	C ₁₇ H ₁₈ N ₆	52	EtOH	223—225	66.46 (66.67)	5.97 (5.88)	27.44 (27.45)
(8e)	Bu ⁱ	C ₁₇ H ₁₈ N ₆	9	EtOH	154—155	66.37 (66.67)	6.10 (5.88)	27.38 (27.45)
(5f)	Oct ⁿ	C ₂₁ H ₂₆ N ₆	52	Oil		69.46 (69.58)	7.24 (7.23)	23.09 (23.19)
(8f)	Oct ⁿ	C ₂₁ H ₂₆ N ₆	24	Oil		69.50 (69.58)	7.29 (7.23)	23.28 (23.19)
(5g)	Ph	C ₁₉ H ₁₄ N ₆	25 ^c	MeOH	144—146 ^b	69.82 (69.92)	4.07 (4.32)	25.76 (25.76)
(8g)	Ph	C ₁₉ H ₁₄ N ₆	12 ^c	MeOH	134—135	69.99 (69.92)	4.27 (4.32)	25.80 (25.76)
(5h)	<i>p</i> -MeC ₆ H ₄	C ₂₀ H ₁₆ N ₆	65 ^c	Me ₂ CO/H ₂ O	183—185	70.55 (70.57)	4.81 (4.74)	24.80 (24.69)
(8h)	<i>p</i> -MeC ₆ H ₄	C ₂₀ H ₁₆ N ₆	4 ^c	MeOH	123—125	70.40 (70.57)	4.80 (4.74)	24.43 (24.69)

^a Lit.²² m.p. 142—143 °C (EtOH) ^b Lit.^{21f}, m.p. 135—137 °C. ^c The yields quoted were for the general method for the preparation of bisbenzotriazolylalkanes. If the general method for the preparation of bis(benzotriazol-1-yl)methylarenes was used the yields observed were 75% for (5g) and 85% for (5h), but no (8g) or (8h) were obtained.

Table 3. ¹H N.m.r. chemical shifts (δ) of 1-(benzotriazol-1-yl)-1-chloroalkanes (2)^a

Compd. no.	R	Aromatic	CHCl	R
(2a)	Me	8.33—8.06 (1 H, m, 4-H) 8.00—7.33 (3 H, m, 5, 6, 7-H)	7.00 (q, <i>J</i> 6 Hz)	2.42 (d, 3 H, Me, <i>J</i> 6 Hz)
(2b)	Et	8.36—8.06 (1 H, m, 4-H) 8.03—7.33 (3 H, m, 5, 6, 7-H)	6.72 (t, <i>J</i> 8 Hz)	2.72 (2 H, m, CH ₂) 1.08 (3 H, t, CH ₃ , <i>J</i> 7 Hz)
(2c)	Pr	8.47—8.12 (1 H, m, 4-H) 8.12—7.38 (3 H, m, 5, 6, 7-H)	6.87 (t, <i>J</i> 8 Hz)	2.72 (2 H, q, CH ₂) 2.48—0.8 (5 H, m, Et)
(2d)	Pr ⁱ	8.40—8.04 (1 H, m, 4-H) 8.04—7.33 (3 H, m, 5, 6, 7-H)	6.48 (d, <i>J</i> 9.2 Hz)	3.5—2.7 (1 H, m, CHMe ₂) 1.38 (3 H, d, CH ₃ , <i>J</i> 7 Hz) 0.85 (3 H, d, CH ₃ , d, CH ₃ , <i>J</i> 7 Hz)
(2e)	Bu ⁱ	8.33—8.04 (1 H, m, 4-H) 8.04—7.25 (3 H, m, 5, 6, 7-H)	6.60 (s)	1.2 (s, Bu ⁱ)
(2f)	Oct	8.35—8.08 (1 H, m, 4-H) 8.07—7.35 (3 H, m, 5, 6, 7-H)	6.8 (t, <i>J</i> 8 Hz)	2.30—3.00 (2 H, m, CH ₂) 2.00—0.60 (15 H, m, hept)

^a In CDCl₃, ref. Me₄Si.

reported for 1,1- and 1,2-bisbenzotriazolylmethanes.^{21d} The methine proton in the aryl substituted compounds (5g), (8g), (5h) and (8h) is deshielded and occurs well downfield at ca. 9.2 p.p.m. The i.r. spectra of the 1-(benzotriazol-1-yl)- and 1-(benzotriazol-2-yl)-1-chloroalkanes (2) and (7), and 1,1-(bisbenzotriazol-1-yl)alkanes (5) and 1-(benzotriazol-1-yl)-1-(benzotriazol-2-yl)alkanes (8) also clearly differentiate the products. Compounds (2) and (5) show two absorptions at ca. 1 610 and 1 590 cm⁻¹, whilst compounds (7) show only one absorption at approximately ca. 1 565 cm⁻¹, and, as expected,

the 1,2-bis adducts (8) show three absorptions at all of the latter positions in accordance with literature reports.²⁶

Mechanism.—Nucleophilic attack of benzotriazole (or its anion) on a protonated carbonyl group occurs to give the 1-hydroxyalkylbenzotriazole (1) which is in equilibrium with its starting materials in solution.¹¹ Reaction with thionyl chloride is irreversible and yields (2) in equilibrium with a small amount of (7). Further reaction with an excess of benzotriazole then yields the bis adducts (5) and (8).

Table 4. ¹³C N.m.r. chemical shifts (δ) of the 1-(benzotriazol-1-yl)-1-chloroalkanes (2)^a

Compd. no.	R	C-3a	C-4	C-5	C-6	C-7	C-7a	CHCl	R
(2a)	Me	146.2	120.0	124.6	128.0	110.2	131.3	66.5	24.2 (CH ₃)
(2b)	Et	146.7	120.2	124.6	128.0	110.3	131.3	72.3	31.1 (CH ₂), 10.7 (CH ₃)
(2c)	Pr	146.1	120.1	124.8	128.1	110.5	131.4	70.7	39.4 (CH ₂), 19.2 (CH ₂), 12.9 (CH ₃)
(2d)	Pr ⁱ	146.7	120.5	124.6	128.1	110.8	131.4	77.6	(CHMe ₂), 20.1 (CH ₃), 19.0 (CH ₃)
(2e)	Bu ⁱ	146.1	120.2	124.3	127.8	111.8	132.5	80.7	(CMe ₃), 26.6 [C(CH ₃) ₃]
(2f)	Oct	146.3	120.1	124.6	128.0	110.4	131.3	71.0	37.6, 31.5, 29.0, 28.8, (Oct) 28.4, 25.9, 22.4, 13.8

^a In CDCl₃, ref. Me₄Si.**Table 5.** ¹H N.m.r. chemical shifts (δ) of the bisbenzotriazoles (5) and (8)^a

Compd. no.	R	Aromatic	CH	R
(5a)	Me ^b	8.36—7.27 (9 H, m)	in aromatic region	2.80 (3 H, d, CH ₃ , <i>J</i> 7 Hz)
(8a)	Me	8.33—7.33 (9 H, m)	in aromatic region	2.75 (3 H, d, CH ₃ , <i>J</i> 7 Hz)
(5b)	Et	8.28—7.22 (9 H, m)	in aromatic region	3.30 (2 H, quin, CH ₂ , <i>J</i> 7 Hz) 1.10 (3 H, t, CH ₃ , <i>J</i> 7 Hz)
(8b)	Et	8.30—7.20 (9 H, m)	in aromatic region	3.27 (2 H, q, CH ₂ , <i>J</i> 7 Hz) 1.02 (3 H, t, CH ₃ , <i>J</i> 7 Hz)
(5c)	Pr	8.30—7.10 (9 H, m)	in aromatic region	3.13 (2 H, q, CH ₂ , <i>J</i> 7 Hz) 1.70—0.72 (5 H, m, Et)
(8c)	Pr	8.32—7.10 (9 H, m)	in aromatic region	3.20 (2 H, CH ₂ , <i>J</i> 7 Hz) 1.80—0.50 (5 H, m, Et)
(5d)	Pr	8.31—7.20 (9 H, m)	in aromatic region	4.49—3.67 (1 H, m, CHMe ₂) 1.05 (6 H, d, Me ₂ , <i>J</i> 6 Hz)
(8d)	Pr ⁱ	8.38—7.40 (9 H, m)	in aromatic region	4.33—3.55 (1 H, m, CHMe ₂)
(5e)	Bu ⁱ	8.33—7.19 (9 H, m)	in aromatic region	1.02 (6 H, d, Me ₂ , <i>J</i> 7 Hz)
(8e)	Bu ⁱ	8.33—7.18 (9 H, m)	in aromatic region	1.42 (9 H, s, Bu ⁱ) 1.38 (9 H, s, Bu ⁱ)
(5f)	Oct	8.30—7.33 (9 H, m)	in aromatic region	3.50—3.00 (2 H, m, CH ₂) 1.66—0.66 (15 H, m, C ₇ H ₁₅)
(8f)	Oct	8.21—7.09 (9 H, m)	in aromatic region	3.39—2.91 (2 H, m, CH ₂) 1.56—0.63 (15 H, m, C ₇ H ₁₅)
(5g)	Ph	8.32—8.0 (2 H, m, 4,4'-H) 7.94—7.07 (11 H, m, 5,5',6,6',7,7'-H,Ph)	9.22 (s)	See aromatic region
(8g)	Ph	8.33—7.75 (3 H, m) 7.66—6.94 (10 H, m)	9.27 (s)	See aromatic region
(5h)	<i>p</i> -MeC ₆ H ₄	8.33—8.00 (2 H, m, 4,4'-H) 7.94—6.94 (10 H, m)	9.17 (s)	2.40 (3 H, s, CH ₃)
(8h)	<i>p</i> -MeC ₆ H ₄	8.43—7.75 (3 H, m) 7.70—6.85 (9 H, m)	9.17 (s)	2.36 (3 H, s, CH ₃)

^a In CDCl₃, ref. Me₄Si. ^b Agrees with literature²²

Slow equilibration between compounds (5) and (8) (see above) and the small amounts of (7) present accounts for the absence of the 2,2-adducts.

Experimental

M.p.s. were determined on a hot-stage microscope and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer Model 283B grating spectrophotometer as thin films (liquids) or mulls (solids). ¹H N.m.r. spectra were recorded on a Varian EM 360L (60 MHz) spectrometer and ¹³C n.m.r. on a Jeol JNM-FX 100 (25.0 MHz) spectrometer for solutions in deuteriochloroform (Me₄Si as internal reference) unless otherwise stated. Mass spectra were recorded at 70 eV on a AEI MS 30 mass spectrometer operating with a DS-55 data system. Elemental analyses were carried out by Dr. R. W. King, University of Florida and Atlanta Microlabs, Georgia. Flash²⁷ and dry column vacuum²⁸ chromatography were carried out using

MCB Silica Gel (230–400 mesh) and Fluka Silical Gel H, respectively.

General Method for the Preparation of 1-(Benzotriazol-1-yl)-1-chloroalkanes.—Thionyl chloride (3 equiv.) was added dropwise at 0 °C to a solution of benzotriazole (1 equiv.) and the aliphatic aldehyde (1.5 equiv.) in chloroform (2 ml/mmol benzotriazole). A white precipitate was formed. The reaction mixture was refluxed for 30 min (40 min in the case of trimethylacetaldehyde) until total dissolution had taken place. On cooling, the reaction mixture was poured into water (2 ml/mmol benzotriazole) and the organic layer separated and washed with 5% aqueous sodium hydrogen carbonate (1 ml/mmol benzotriazole). After drying (MgSO₄), the solvent was removed and the crude product subjected to chromatography.

(a) *Acetaldehyde.* 1-(Benzotriazol-1-yl)-1-chloroethane (2a) was isolated as an oil (55%) (Table 1) and characterised by elemental analysis (Table 1) and spectroscopic methods: ν_{\max} 1 615 and 1 595 cm⁻¹; ¹H n.m.r. (Table 3) and ¹³C n.m.r. (Table 4).

Table 6. ^{13}C N.m.r. chemical shifts (δ) of the bisbenzotriazoles (**5**) and (**8**)^a

Compd. no.	R	C-3a ^b	C-4 ^c	C-5 ^d	C-6	C-7	C-7a	CH	R
(5a)	Me	146.6	120.1	124.7	128.4	110.1	131.5	68.0	18.3 (Me)
(8a)	Me	146.4 (144.3)	120.1 (118.4)	124.5 (127.3)	128.1	110.4	132.0	73.3	19.0 (Me)
(5b)	Et	146.3	120.0	124.5	128.2	110.0	131.5	72.9	25.0 (CH ₂), 9.9 (CH ₃)
(8b)	Et	146.1 (144.1)	119.8 (118.2)	124.2 (127.0)	127.8	110.4	131.8	78.3	25.8 (CH ₂), 9.5 (CH ₃)
(5c)	Pr	146.4	120.1	124.6	128.3	110.1	131.6	71.4	33.3 (CH ₂), 18.8 (CH ₂), 13.1 (CH ₃)
(8c)	Pr	146.3 (144.3)	120.0 (118.4)	124.3 (127.1)	128.0	110.6	132.0	77.0	34.2 (CH ₂), 18.4 (CH ₂), 13.1 (CH ₃)
(5d)	Pr ⁱ	146.3	120.1	124.7	128.4	110.3	132.0	77.1	30.3 (CHMe ₂), 19.1 ((CH ₃) ₂ CH)
(8d)	Pr ⁱ	146.5 (144.4)	120.7 (118.6)	124.5 (127.3)	128.2	111.1	132.1	83.6	31.5 (CHMe ₂) 18.9 (CH ₃), 18.6 (CH ₃)
(5e)	Bu ⁱ	145.8	120.0	124.5	128.3	110.8	132.8	79.7	39.3 (CMe ₃), 27.2 (Me ₃ C)
(8e)	Bu ⁱ	145.7 (144.1)	120.1 (118.6)	124.3 (127.2)	128.0	111.2	133.1	85.0	38.9 (CMe ₃), 27.1 (Me ₃ C)
(5f)	Oct	146.2	119.8	124.4	128.1	110.0	131.4	71.5	31.3, 31.2, 28.8, 28.7, 18.4, 25.1, 22.2, 13.7 (n-Oct)
(8f)	Oct	146.4 (144.4)	120.1 (118.5)	124.4 (127.3)	128.1	110.7	132.1	77.4	32.5, 31.6, 29.1, 29.0, 28.7, 25.2, 22.5, 14.0 (n-Oct)
(5g)	Ph	145.9	119.9	124.5	128.2	110.5	132.1	72.2	129.5, 128.6, 126.8 (Ph)
(8g)	Ph	146.5 (144.4)	120.0 (118.5)	124.3 (127.3)	128.8	112.2 110.9	132.6 132.5	79.3 78.4	129.7, 128.0, 126.7 (Ph) 140.0, 129.8, 127.0, 129.4
(5h)	<i>p</i> -MeC ₆ H ₄	146.3	120.2	124.7	128.4	112.5	132.4	79.6	140.1, 129.9, 126.9, 129.7
(8h)	<i>p</i> -MeC ₆ H ₄	146.8 (144.6)	120.1 (118.7)	124.4 (127.4)	128.0				

^a In CDCl₃, ref. Me₄Si. ^b Figures in brackets refer to C-3a', 7a'. ^c Also refers to C-4', 7'. ^d Also refers to C-5', 6'.

(b) *Propionaldehyde*. 1-(Benzotriazol-1-yl)-1-chloropropane (**2b**) was isolated as an oil (52%) (see Table 1) and characterised by elemental analysis (Table 1) and spectroscopic methods: ν_{max} . 1 610 and 1 590 cm⁻¹; ¹H n.m.r. (Table 3) and ¹³C n.m.r. (Table 4).

(c) *n-Butyraldehyde*. 1-(Benzotriazol-1-yl)-1-chlorobutane (**2c**) was isolated as an oil (100%) (see Table 1) and characterised by spectroscopic methods: ν_{max} . 1 615 and 1 595 cm⁻¹; ¹H n.m.r. (Table 3) and ¹³C n.m.r. (Table 4). Full purification of this compound was not carried out due to its partial decomposition to 1-(2-methylbut-1-enyl)benzotriazole (**6b**; R' = Me), b.p. 108–109 °C/0.1 mmHg, when kept at 20 °C or when heated; ν_{max} . 1 615 and 1 595 cm⁻¹; ¹H n.m.r. (Table 3) and ¹³C n.m.r. (Table 4). A pure sample of the latter compound was obtained after two vacuum distillations (Found: C, 69.15; H, 6.45; N, 24.15. C₁₀H₁₁N₃ requires C, 69.34; H, 6.40; N, 24.26%; ν_{max} . 1 675, 1 610, and 1 590 cm⁻¹; δ_{H} (60 MHz; CDCl₃); 1.20 (3 H, t, CH₃, *J* 7 Hz), 2.35 (2 H, q, CH₂, *J* 7 Hz), 7.18–7.90 (3 H, m, s, 6, 7-H), and 8.04–8.32 (1 H, m, 4-H); δ_{C} (25 MHz; CDCl₃) 13.1 (CH₃), 20.8 (CH₂), 109.7 (7-C), 119.5 (4-C), 121.9 (CH=CH₂), 123.9 (N-CH=CH₂), 124.5 (5-C), 127.4 (6-C), 131.0 (7a-C), 145.7 (3a-C).

(d) *Isobutyraldehyde*. Separation by dry column vacuum chromatography using dichloromethane as the solvent, followed by recrystallisation, yielded 1-(benzotriazol-1-yl)-1-chloro-2-methylpropane (**2d**) (51%) characterised by elemental analysis (Table 1) and spectroscopic methods; ν_{max} . 1 610 and 1 590 cm⁻¹; ¹H n.m.r. (Table 3), ¹³C n.m.r. (Table 4), and mass spectroscopy [*m/z* 209 (*M*⁺, 2%), 174 (47), 144 (18), 130 (26), 104 (100), 91 (35), 77 (58), 55 (67), 41 (49), and 36 (70)]. 1-(2-Methylpropenyl)benzotriazole (**6a**; R' = Me) (29%), m.p. 69–71 °C (lit.,²⁹ 70–71 °C), was also isolated. Spectroscopic properties agreed well with those reported in the literature.²⁹

(e) *Trimethylacetaldehyde*. Separation by dry column vacuum chromatography using dichloromethane as the solvent followed

by recrystallisation yielded 1-(benzotriazol-1-yl)-1-chloro-2,2-dimethylpropane (**2e**) (82%) (Table 1) characterised by elemental analysis (Table 1); ν_{max} . 1 610 and 1 585 cm⁻¹; ¹H n.m.r. (Table 3), ¹³C n.m.r. (Table 4), and mass spectroscopy [*m/z* 223 (*M*⁺, 3%), 188 (100), 166 (27), 140 (23), 138 (69), 118 (28), 111 (36), 104 (74), 77 (25), 76 (21), 70 (25), 69 (21), 57 (52), and 41 (42)]. Traces of the 2-chloro compound (**7e**) and bis adducts (**5e**) and (**8e**) were also present in the crude reaction mixture.

(f) *Nonanal*. 1-(Benzotriazol-1-yl)-1-chlorononane (**2f**) (98%) (see Table 1) was characterised by elemental analysis (Table 1) and spectroscopic methods: ν_{max} . 1 615 and 1 590 cm⁻¹; ¹H n.m.r. (Table 3) and ¹³C n.m.r. (Table 4).

Preparation of (3e; Nu = CN).—1-(Benzotriazol-1-yl)-1-chloro-2,2-dimethylpropane (**2e**) (0.22 g, 1 mmol) and sodium cyanide (0.045 g, 0.9 mmol) were heated in dimethyl sulphoxide (2 ml) at 50 °C for 15 h. Chromatography of the crude material using benzene–chloroform (1:1) as the eluant yielded 2-(benzotriazol-1-yl)-3,3-dimethylbutyronitrile (**3e**, Nu = CN) (0.14 g, 6.6 mmol, 74%), m.p. 122–123 °C, after recrystallization from pentane (Found: C, 67.3; H, 6.85; N, 26.15. C₁₂H₁₄N₄ requires C, 67.26; H, 6.58; N, 26.15%; δ_{H} (60 MHz; CDCl₃) 1.20 (9 H, s, Buⁱ), 5.73 (1 H, s, CH), 7.23–7.89 (3 H, m, s, 6, 7-H), and 8.10–8.50 (1 H, m, 4-H).

Preparation of (3c; Nu = PhCO₂).—1-(Benzotriazol-1-yl)-1-chlorobutane (**2c**) (2.10 g, 10 mmol) and sodium benzoate (1.30 g, 9 mmol) were heated at 50 °C for 2 h in dimethyl sulphoxide (10 ml) and then kept at room temperature for 15 h. The reaction mixture was poured into water (10 ml) and extracted with ether (3 × 5 ml). The ether solution was washed with water (5 ml), dried (MgSO₄), and evaporated. The crude product was purified by chromatography using benzene–chloroform (1:1) to yield an oil, 1-(benzotriazol-1-yl)-1-butylbenzoate (**3c**; Nu = PhCO₂) (2.42 g, 8.19 mmol, 91%) (Found: *M*⁺, 295.1308.

$C_{17}H_{17}N_3O_2$ requires M , 295.1320 δ_H (60 MHz; $CDCl_3$) 0.66—1.66 (5 H, m, Et), 2.33—2.90 (2 H, q, CH_2 , J 7.2 Hz), and 7.1—8.5 (10 H, m, ArH CH).

Preparation of (3c; Nu = PhS).—Sodium (0.202 g, 9 mmol) was added to thiophenol (0.99 g, 9 mmol) in methanol (10 ml) under a nitrogen atmosphere. When the sodium had dissolved 1-(benzotriazol-1-yl)-1-chlorobutane (**2c**) (2.09 g, 10 mmol) was added and the reaction mixture stirred for 10 h at room temperature. The reaction mixture was poured into water and extracted with chloroform and the solution dried ($MgSO_4$) and evaporated. The crude product was purified by chromatography (benzene-chloroform 1:1) to yield 1-(benzotriazol-1-yl)-1-thienylbutane (**3c**; Nu = PhS) (2.25 g, 88%) (Found: C, 67.6; H, 6.05, N, 14.75. $C_{16}H_{17}N_3S$ requires C, 67.81; H, 6.05; N, 14.83%); δ_H (60 MHz; $CDCl_3$) 0.66—1.83 (5 H, m, Et), 2.19—2.73 (2 H, q, CH_2 , J 8 Hz), 6.20 (1 H, t, CH, J 8 Hz), and 8.19—7.03 (9 H, m, ArH).

General Method for the Preparation of Bis(benzotriazolyl)alkanes.—Thionyl chloride (3 equiv.) was added slowly dropwise at 0 °C to benzotriazole (2 equiv.) and the aliphatic aldehyde (1 equiv.). The reaction mixture was refluxed for 1—1.5 h. On cooling, chloroform (1 ml/mmol benzotriazole) was added and the solution washed with water (2 × 0.5 ml/mmol benzotriazole), 5% aqueous sodium hydrogen carbonate (0.5 ml/mmol benzotriazole), and water (0.5 ml/mmol benzotriazole). The organic layer was dried ($MgSO_4$), evaporated and the crude product separated by chromatography.

Acetaldehyde. Separation by flash chromatography using ethyl acetate—light petroleum (b.p. 40—60 °C) yielded four fractions: 1-(benzotriazol-2-yl)-1-chloroethane (**7a**) (2%), v_{max} 1 565 cm^{-1} ; δ_H (60 MHz; $CDCl_3$) 2.36 (3 H, d, CH_3 , J 7 Hz), 6.90 (1 H, q, CH), and 7.20—8.30 (4 H, m, 4, 5, 6, 7-H); 1-(benzotriazol-1-yl)-1-chloroethane (**2a**) (3%) was identified by i.r. and n.m.r. spectroscopy, 1-(benzotriazol-1-yl)-1-(benzotriazol-2-yl)ethane (**8a**) (5%) (Table 2), v_{max} 1 615, 1 595, and 1 565 cm^{-1} ; 1H n.m.r. (Table 5) and ^{13}C n.m.r. (Table 6), and mass spectroscopy [Found: M^+ 264.1130. $C_{14}H_{12}N_6$ requires 264.1123; m/z 264 (M^+ , 14%), 180 (13), 146 (100), 119 (15), 118 (40), 117 (46), 97 (57), and 90 (14)], and 1,1-bis(benzotriazol-1-yl)ethane (**5a**) (32%) identified by elemental analysis (Table 2), i.r. v_{max} 1 615 and 1 595 cm^{-1} ; 1H n.m.r. (Table 5), ^{13}C n.m.r. (Table 6), and mass spectroscopy m/z 264 (M^+ , 3%), 185 (25), 180 (20), 149 (99), 146 (44), 119 (52), 118 (36), 117 (60), 97 (46), 91 (78), and 43 (100).

Propionaldehyde. Separation by flash chromatography using ethyl acetate—light petroleum (b.p. 40—60 °C) (15:85) as the solvent yielded four fractions. The first fraction was shown to be 1-(benzotriazol-2-yl)-1-chloropropane (**7b**) (1%), v_{max} 1 560 cm^{-1} ; δ_H (60 MHz; $CDCl_3$) 1.05 (3 H, t, CH_3 , J 6 Hz), 2.55—2.98 (2 H, m, CH_2), 6.64, (1 H, t, CH, J 6 Hz), 7.33—7.68 (2 H, m, 5, 6-H), 7.73—8.15 (2 H, m, 4, 7-H). The second fraction yielded (**2b**) (0.5%) as indicated by 1H n.m.r. spectroscopy. The third fraction yielded pure 1-(benzotriazol-1-yl)-1-(benzotriazol-2-yl)propane (**8b**) (13%) (Table 2) after recrystallisation; v_{max} 1 610, 1 590, and 1 560 cm^{-1} ; 1H n.m.r. (Table 5), ^{13}C n.m.r. (Table 6) and m/z 278 (M^+ ; 12%), 161 (11), 160 (100), 132 (42), 117 (34), 105 (12), 104 (25), 91 (18), 90 (19), 77 (45), 64 (11), and 41 (17). The fourth fraction gave pure 1,1-bis(benzotriazol-1-yl)propane (**5d**) (60%) after recrystallisation (Table 2); v_{max} 1 610 and 1 585 cm^{-1} ; 1H n.m.r. (Table 5); ^{13}C n.m.r. (Table 6); m/z 278 (M^+ , 10%), 250 (7), 221 (8), 192 (7), 161 (11), 160 (100), 132 (50), 130 (9), 117 (39), 105 (10), 104 (30), 103 (13), 91 (19), 90 (22), 77 (60), 76 (17), 51 (11), 50 (11), and 39 (13).

Butyraldehyde. Separation by flash chromatography using ethyl acetate—light petroleum ether (b.p. 40—60 °C) gave four fractions. The first fraction, an oil, was shown to be 1-

(benzotriazol-1-yl)-1-chlorobutane (**7c**) (2%); v_{max} 1 565 cm^{-1} , δ_H (60 MHz; $CDCl_3$) 0.75—2.90 (7 H, m, Pr), 6.66 (1 H, t, CH, J 7 Hz), 7.25—7.68 (2 H, m, 5, 6-H), 7.80—8.20 (2 H, m, 4, 7-H). The second fraction, 1-(1-benzotriazolyl)-1-chlorobutane (**2c**) (1%), was identified spectroscopically. The third fraction was shown to be 1-(benzotriazol-1-yl)-1-(benzotriazol-2-yl)butane (**8c**) (14%) (Table 2); v_{max} 1 615, 1 590, and 1 565 cm^{-1} ; 1H n.m.r. (Table 5); ^{13}C n.m.r. (Table 6) m/z 292 (M^+ , 14%), 264 (7), 174 (100), 146 (18), 131 (10), 118 (21), 117 (11), and 104 (70). The fourth fraction, a white crystalline solid, was identified as 1,1-bis(benzotriazol-1-yl)butane (**5c**) (29%) (Table 2); v_{max} 1 615 and 1 590 cm^{-1} ; 1H n.m.r. (Table 5); ^{13}C n.m.r. (Table 6) m/z 292 (M^+ , 7%), 264 (6), 174 (100), 146 (24), 131 (8), 118 (17), 117 (13), 104 (74), 103 (11), 91 (21), 77 (44), 76 (14), and 50 (7).

Isobutyraldehyde. Separation by dry column vacuum chromatography using ethyl acetate—light petroleum (b.p. 40—60 °C) yielded four fractions. The first fraction was shown to be 1-(benzotriazol-2-yl)-1-chloro-2-methylpropane (**7d**) (<3%) δ_H (60 MHz; $CDCl_3$) 0.98 (3 H, d, CH_3 , J 7 Hz), 1.32 (3 H, d, CH_3 , J 7 Hz), 2.63—3.50 (1 H, m, $CHMe_2$), 6.38 (1 H, d, $CHPr$, J 9 Hz), 7.30—7.70 (2 H, m, 5, 6-H), and 7.88—8.30 (2 H, m, 4, 7-H); δ_C (25 MHz; $CDCl_3$) 18.7 (CH_3), 19.3 (CH_3), 36.5 ($CHMe_2$), 82.1 ($CHPr$), 118.5 (4, 7-C), 127.4 (5, 6-C), and 145.2 (3a, 7a-C). The second fraction consisted of trace amounts of a mixture of (**2d**) and (**6a**; $R' = Me$). The third fraction, a white crystalline solid, was characterized as 1-(benzotriazol-1-yl)-1-(benzotriazol-2-yl)-2-methylpropane (**8d**) (18%) (Table 2); v_{max} 1 610, 1 590, and 1 560 cm^{-1} ; 1H n.m.r. (Table 5); ^{13}C n.m.r. (Table 6); m/z 292 (M^+ , 10%), 264 (1), 249 (5), 221 (3), 174 (100), 120 (13), 104 (55), 91 (25), 77 (24), and 28 (7). The fourth fraction, a white solid, was shown to be 1,1-bis(benzotriazol-1-yl)-2-methylpropane (**5d**) (41%) (Table 2); v_{max} 1 610 and 1 590 cm^{-1} ; 1H n.m.r. (Table 5); ^{13}C n.m.r. (Table 6); m/z 292 (M^+ , 18%), 264 (12), 249 (65), 221 (52), 192 (43), 174 (100), 118 (14), 104 (96), 91 (67), 77 (69), and 28 (24).

Trimethylacetaldehyde. Dry column vacuum chromatography using ethyl acetate—light petroleum (b.p. 40—60 °C) (1:9) gave four fractions. Fraction one, a colourless oil, was identified as 1-(benzotriazol-2-yl)-1-chloro-2,2-dimethylpropane (**7e**) (<2%) δ_H (60 MHz; $CDCl_3$) 1.22 (9 H, s, Bu^t), 6.53 (1 H, s, CH), 7.30—7.77 (2 H, m, 5, 6-H), 7.8—8.16 (2 H, m, 4, 7-H); δ_C (25 MHz; $CDCl_3$) 26.0 [$(CH_3)_3C$], 39.1 (CMe_3), 85.1 (CH), 118.5 (4, 7-C) 127.3 (5, 6-C), and 144.1 (3a, 7a-C). Fraction two was shown to be (**2e**) (3%) by 1H n.m.r. spectroscopy. Fraction three yielded white crystals of 1-(benzotriazol-1-yl)-1-(benzotriazol-2-yl)-2,2-dimethylpropane (**8e**) (9%); elemental analysis (Table 2); v_{max} 1 610, 1 590, and 1 560 cm^{-1} ; 1H n.m.r. (Table 5); ^{13}C n.m.r. (Table 6); m/z 306 (M^+ , 3%), 249 (41), 222 (16), 192 (24), 188 (43), 166 (100), 120 (45), 91 (34), 77 (34), 57 (49), 41 (95), and 28 (100). Fraction four, white crystals, was characterised as 1,1-bis(benzotriazol-1-yl)-2,2-dimethylpropane (**5e**) (52%) elemental analysis (Table 2) v_{max} 1 610—1 590 cm^{-1} br; 1H n.m.r. (Table 5); ^{13}C n.m.r. (Table 6) m/z 306 (M^+ , 2%), 278 (1), 249 (100), 221 (75), 192 (72), 166 (51), 103 (97), 76 (71), 57 (78), 41 (70), and 28 (20).

Nonanal. Chromatography, using ethyl acetate—light petroleum ether (b.p. 40—60 °C) (1:9) as the solvent, yielded five fractions. The first fraction, a light-yellow oil, was 1-(benzotriazol-2-yl)-1-chlorononane (**7f**) (6%) v_{max} 1 565 cm^{-1} ; δ_H (60 MHz; $CDCl_3$) 0.66—1.70 (15 H, m, C_7H_{15}), 2.30—3.00 (2 H, m, CH_2), 6.70 (1 H, t, CH), 7.27—7.62 (2 H, m, 5, 6-H), 7.75—8.09 (2 H, m, 4, 7-H); δ_C (25 MHz; $CDCl_3$) 14.1, 22.6, 25.8, 28.7, 29.1, 29.2, 31.8, 38.3 (octyl), 76.2 (CH) 118.6 (4, 7-C), 127.6 (5, 6-C), and 144.7 (C-3a, 7a). The second yellow oil isolated was (**2f**) (9%) as indicated by 1H n.m.r. spectroscopy. The third fraction, an oil, was shown to be 1-(non-1-enyl)benzotriazole (**6i**; $R' = H$) (4%), v_{max} 1 450, 1 590, 1 610, and 1 670 cm^{-1} ; δ_H (60 MHz; $CDCl_3$) 0.59—1.70 (13 H, m, C_7H_{13}), 2.03—2.50 (2 H, m, CH_2),

6.27—6.81 (1 H, q, CH), 7.15—7.83 (4 H, m, 4, 5, 6-H, CH), and 8.00—8.30 (1 H, m, 7-H)]. The fourth fraction, a light yellow oil, was shown to be 1-(benzotriazol-1-yl)-1-(benzotriazol-2-yl)nonane (**8f**) (24%) (see Table 2); ν_{\max} . 1 610, 1 590, and 1 560 cm^{-1} ; ^1H n.m.r. (Table 5); ^{13}C n.m.r. (Table 6); Found: M^+ 362.2199. $\text{C}_{21}\text{H}_{26}\text{N}_6$ requires 362.2222; m/z 362 (M^+ , 1%), 245 (16), 246 (95), 243 (15), 216 (52), 166 (12), 132 (16), 130 (14), 120 (39), 119 (26), 118 (16), 117 (12), 104 (100), 91 (36), 81 (13), 77 (38), 69 (16), 67 (13), 65 (12), 64 (13), 55 (34), and 41 (55). The fourth fraction yielded 1,1-(bisbenzotriazol-1-yl)nonane (**5f**) (52%) (Table 2) ν_{\max} . 1 610, 1 590 cm^{-1} ; ^1H n.m.r. (Table 5); ^{13}C n.m.r. (Table 6); m/z 362 (M^+ , 1%), 245 (12), 244 (71), 243 (10), 221 (13), 216 (41), 192 (10), 132 (14), 130 (11), 119 (10), 118 (13), 117 (11), 105 (11), 104 (100), 103 (15), 91 (21), 77 (43), 76 (13), 57 (10), 55 (32), 46 (26), 41 (33), and 29 (18).

General Method for the Preparation of Bis(benzotriazol-1-yl)methylarenes.—The method used was the same as for the bisbenzotriazolylalkanes, except that after a period of 1—1.5 h under reflux, the excess of thionyl chloride was distilled off and benzene added to remove the final traces after distillation. The solid was washed with hexane and then recrystallised to give the product.

Benzaldehyde. Bis(benzotriazol-1-yl)methylbenzene (**5g**) (75%) elemental analysis (Table 2), ν_{\max} . 1 610 and 1 590 cm^{-1} ; ^1H n.m.r. (Table 5); ^{13}C n.m.r. (Table 6); m/z 326 (M^+ , 1%), 209 (11), 208 (69), 181 (17), 180 (100), 153 (23), 152 (43), 151 (12), 77 (24), 51 (14), and 28 (43).

p-Tolualdehyde. p-Bis(benzotriazol-1-yl)methyltoluene (**5h**) (85%) (Table 2); ν_{\max} . 1 615 and 1 590 cm^{-1} ; ^1H n.m.r. (Table 5); ^{13}C n.m.r. (Table 6); m/z 340 (M^+ , 1%), 223 (11), 222 (65), 195 (16), 194 (100), 193 (11), 192 (10), 167 (13), 165 (14), 152 (14), and 77 (18).

If the reaction work-up was changed to that used for the bisbenzotriazolylalkanes, (benzotriazol-1-yl)(benzotriazol-2-yl)methylbenzene (**8g**), 12% and p-(benzotriazol-1-yl)(benzotriazol-2-yl)methyltoluene (**8h**) (4%) (Table 2) could be isolated along with (**5g**) and (**5h**) respectively. However, this method resulted in hydrolysis of some of the product back to starting materials. Compounds (**8g**) and (**8h**) were characterised by i.r. ν_{\max} . 1 615, 1 590, and 1 565 cm^{-1} ; ^1H n.m.r. (Table 5); ^{13}C n.m.r. (Table 6) and m.s.: (**8g**) [m/z 326 (M^+ , 2%), 209 (13), 208 (78), 181 (16), 180 (100), 153 (22), 152 (41), 77 (33), 51 (13)]; and (**8h**) [m/z 340 (M^+ , 1%), 223 (10), 222 (61), 195 (16), 194 (100), 193 (17), 192 (11), 167 (15), 166 (11), 165 (23), 152 (24), 91 (19), 77 (25), 65 (12), 63 (11), and 39 (12)].

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