The first examples of the addition of heterocyclic NH to unactivated olefins

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Benzotriazole adds to aliphatic open-chain and cyclic alkenes at 80 °C under toluene-*p*-sulfonic acid catalysis. Terminal aliphatic olefins give solely 2-(benzotriazol-1- and -2-yl)alkanes, which are stable to acid. In the presence of an excess of acid, all possible non-terminal benzotriazol-1- and -2-yl addition products are obtained, owing to a facile migration of the double bond in the starting olefin. Addition also occurs to phenylalkenes with the intervention of some bond migration.

Introduction

Michael additions of NH-functionality to electron-deficient olefins are among the best known reactions of organic chemistry. In contrast, very few analogous additions to unactivated olefins have been reported, and most involve extreme temperature and pressure. For example, ammonia, ethylene, ammonium iodide and water heated at 330 °C/2800 psig for 5 h gave 49% ethylamine, 10% diethylamine and 2% triethylamine.[1] Isobutene and ammonia, passed over chromo-nitrate-impregnated Pentasil-type borosilicate at 300 °C/300 bar, yielded 15% of *tert*-butylamine.[2] Styrene and piperidine form *N*-phenethylpiperidine using sodium as a catalyst in an autoclave after 6 h at 200 °C in 81% yield, however, dibutylamine and styrene under the same conditions gave only 25% of 1-(*N*,*N*-dibutylamino)-2-phenylethane.[3] Carbazole forms an adduct with stilbene in 18% yield when the mixed crystal is irradiated with ultraviolet light.[4] Additions of NH-groups of *N*-heterocycles to unactivated olefins are apparently unreported in the literature.

We have previously found that benzotriazole adds readily to electron-deficient (*e.g.*, crotonaldehyde, acrolein)[5] and electron-rich olefins (*e.g.*, vinyl ether).[6] We now report that benzotriazole also reacts with unactivated olefins under acid catalysis to give the corresponding addition products in good yield.

Results

Terminal alkenes were treated with benzotriazole (BtH) **1** and 0.1 molar equivalent of toluene-*p*-sulfonic acid in a sealed tube warmed to 80 °C. In all cases benzotriazole added across the double bond to provide alkylbenzotriazoles in good yield (see Fig. 1).

In the alkylbenzotriazole products, the benzotriazolyl group was always located at position 2 of the alkyl chain, except in the cases of highly branched or phenyl-substituted olefins, where the products resulted from prior acid-catalysed rearrangements of the starting olefin. Mixtures of 2-(benzotriazol-1- and -2-yl)alkanes were formed in each system, however these pairs of isomers were readily separated on the basis of their difference in pK_a.[7] In concentrated (10 mol dm^{-3}) aqueous HCl, the benzotriazol-1-yl (Bt-1) isomer is protonated and therefore soluble in the aqueous phase, allowing the extraction of only the benzotriazol-2-yl (Bt-2) isomer into the organic phase. Dilution of the acid solution with water followed by further extraction provided the Bt-1 isomer. This technique allowed the separation of each isomer to greater than 90% purity. Products resulting from the addition of benzotriazole to phenyl substituted alkenes were sometimes crystalline, which facilitated purification.

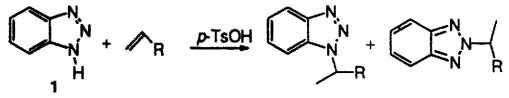

Fig. 1 The reaction of benzotriazole with terminal olefins and toluene-*p*-sulfonic acid

In another series of reactions, the addition was carried out in the presence of one molar equivalent of toluene-*p*-sulfonic acid. In the cases where double bond migration could occur, a mixture of all possible positional isomers was obtained, and for every position of addition to the alkene substrate, both Bt-1 and Bt-2 isomers were formed. The acid washing technique described above was used initially to separate the complex mixtures into two fractions, the first of which was composed of the isomeric benzotriazol-1-ylalkanes, and the other of the corresponding benzotriazol-2-yl analogues. Further attempts to separate the resulting two, three or four component mixtures by column chromatography or HPLC (normal phase silica) were unsuccessful. Separation of these mixtures was achieved on the basis of boiling point using preparative gas chromatography. This technique produced either pure single compounds, or mixtures of two components which could then be readily identified by NMR spectroscopy. The NMR based structural assignments are also supported by analysis of the GC–MS cracking pattern data, which can be used to determine the structure of alkylbenzotriazoles.[8]

Addition of BtH to phenylalkenes

Three homologous phenylalkenes were reacted with BtH under the above conditions, with results as summarized in Table 1 (see Fig. 2). The reaction of BtH with styrene and 10 mol% toluene-*p*-sulfonic acid produced a 6.5:1 mixture of 1-(benzotriazol-1-yl)-1-phenylethane **2a** and 1-(benzotriazol-2-yl)-1-phenylethane **2b** in 46% isolated yield; the two isomers were separated by column chromatography, and characterized by microanalysis (Table 1) and spectroscopy (Tables 6 and 7 in the Supplementary Material).† Under the alternative reaction conditions of 1 molar equivalent of toluene-*p*-sulfonic acid, the isolated yield improved to 50%; however, more of the Bt-2 isomer was produced (see Table 1).

Allylbenzene and BtH, even with 10 mol% toluene-*p*-sulfonic acid, produced a mixture of positional isomers resulting from isomerization of the starting alkene, as well as the expected

† Suppl. Pub. 57098 (5 pp.). For details of the British Library Supplementary Publications scheme see 'Instructions for Authors (1995)', *J. Chem. Soc., Perkin Trans. 2*, 1995, issue 1.

Table 1 Properties of addition products of BtH to styrene and to allylbenzene

Product	t_R/min	Yield (%)[a] 10[b]	Yield (%)[a] 100[b]	Formula	Found (%) (Required) C	H	N
Mixture of **2a** and **2b**	—	45.9	49.5		(75.31)	(5.87)	(18.82)
1-(Benzotriazol-1-yl)-1-phenylethane **2a**	22.3	(39.8)	(32.2)	$C_{14}H_{13}N_3$	75.36	5.97	18.99
1-(Benzotriazol-2-yl)-1-phenylethane **2b**	20.7	(6.1)	(17.3)	$C_{14}H_{13}N_3$	75.19	5.99	19.02
					(75.92)	(6.37)	(17.71)
Mixture of **3a**, **3b**, **3c** and **3d**	—	65.8	71.4	$C_{15}H_{15}N_3$	75.85	6.42	17.85
1-(Benzotriazol-1-yl)-1-phenylpropane **3a**	24.1	(18.6)	(24.5)	$C_{15}H_{15}N_3$	76.17	6.43	17.71
2-(Benzotriazol-1-yl)-1-phenylpropane **3b**	24.3	(23.3)	(27.4)	$C_{15}H_{15}N_3$	—	—	—
1-(Benzotriazol-2-yl)-1-phenylpropane **3c**[c]	20.7	(13.3)	(5.8)	$C_{15}H_{15}N_3$	75.87	6.39	17.70
2-(Benzotriazol-2-yl)-1-phenylpropane **3d**[c]		(10.6)	(13.7)				

[a] Isolated yield, GC yields in parentheses. [b] Mol% toluene-*p*-sulfonic acid used. [c] Compounds **3c** and **3d** were not resolved by capillary GC, relative amounts of **3c** and **3d** determined by ^{1}H NMR spectroscopy.

Table 2 Properties of isomeric benzotriazolyl(phenyl)butanes

Product	t_R/min	Yield (%)[b] 10[c]	Yield (%)[b] 100[c]
Mixture of **4a–4f**[a]		65.0	61.7
1-(Benzotriazol-1-yl)-1-phenylbutane **4a**	23.5	(0)	(10.6)
2-(Benzotriazol-1-yl)-1-phenylbutane **4b**	23.1	(0)	(5.7)
3-(Benzotriazol-1-yl)-1-phenylbutane **4c**	24.5	(42.7)	(10.0)
1-(Benzotriazol-2-yl)-1-phenylbutane **4d**	21.7	(0)	(4.2)
2-(Benzotriazol-2-yl)-1-phenylbutane **4e**	21.5	(0)	(6.0)
3-(Benzotriazol-2-yl)-1-phenylbutane **4f**	19.6	(22.3)	(25.2)

[a] Satisfactory GC–HRMS data obtained for each isomer, *e.g.*, **4a** (Found: M^+, 251.1418. $C_{16}H_{17}N_3$ requires for *M*, 251.1422). [b] Isolated yield, GC yields in parentheses. [c] Mol% toluene-*p*-sulfonic acid used.

Table 3 Properties of isomeric addition products of BtH to pent-1-ene

Product[a]	t_R/min	Yield (%)[b] 10[c]	Yield (%)[b] 100[c]
Mixture of **5a–5c**	—	18.2	23.4
2-(Benzotriazol-1-yl)pentane **5a**	18.68	(16.7)	(16.5)
3-(Benzotriazol-1-yl)pentane **5b**	18.10	(1.5)	(3.8)
2-(Benzotriazol-1-yl)-2-methylbutane **5c**	18.60	(0)	(3.1)
Mixture of **5d–5f**	—	9.1	15.2
2-(Benzotriazol-2-yl)pentane **5d**	16.29	(9.1)	(9.2)
3-(Benzotriazol-2-yl)pentane **5e**	15.77	(0)	(3.4)
2-(Benzotriazol-2-yl)-2-methylbutane **5f**	15.91	(0)	(2.6)

[a] Elemental analysis was performed on the mixture **5a–f** in the reaction using 100 mol% TsOH (Found: C, 69.51; H, 7.94; N, 22.87. Calc. for $C_{11}H_{15}N_3$: C, 69.81; H, 7.99; N, 22.20%). [b] Isolated yield, GC yields in parentheses. [c] mol% toluene-*p*-sulfonic acid used.

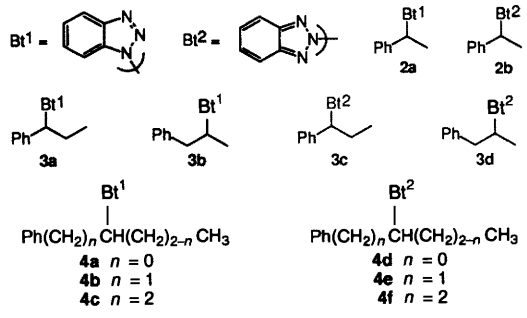

Fig. 2 Products of the addition of benzotriazole to phenylalkenes

mixture of Bt-1 and Bt-2 isomers (see Table 1). After acidic separation of the mixture into Bt-1 and Bt-2 fractions, the two Bt-1 components **3a** and **3b** were separated by crystallization. The Bt-2 fraction also contained two positional isomers **3c** and **3d** which could not be separated by crystallization, chromatography, or preparative GC. However, the identities and relative proportions of the two isomers were readily determined by ^{1}H NMR spectroscopy, and the mixture gave a satisfactory microanalysis (see Table 1 for CHN results, and Tables 6 and 7 in the supplementary material for NMR spectral data). When 1 molar equivalent of acid was employed, the overall yield improved, and a similar mixture of isomers was obtained.

4-Phenyl-1-butene produced in 65% yield a 2:1 mixture of 3-(benzotriazol-1-yl)-1-phenylbutane **4c** and 3-(2-benzotriazolyl)-1-phenylbutane **4f** with 10 mol% toluene-*p*-sulfonic acid, and a complex mixture of all possible isomers when 100 mol% toluene-*p*-sulfonic acid was present (see Table 2). 3-(Benzotriazol-2-yl)-1-phenylbutane **4f** was separated from the former reaction mixture by column chromatography. The remaining components of the mixture could not be separated by this means and were identified by GC–MS.

Addition of BtH to *n*-alkenes

Benzotriazole was similarly reacted with pent-1-ene, oct-1-ene, and dec-1-ene under the standard conditions (see Fig. 3). Reaction of pent-1-ene with 10 mol% toluene-*p*-sulfonic acid produced the expected mixture of 2-(benzotriazol-1- and -2-yl)pentane in 27% combined yield (see Table 3). With 1 molar equivalent of toluene-*p*-sulfonic acid, 39% of a complex mixture of all four non-terminal Bt-1 and Bt-2 substituted isomers was produced, along with 2-(benzotriazol-1- and -2-yl)-2-methylbutane resulting from prior rearrangement of the pentene carbon skeleton (see Table 3). The mixture **5a–f** was separated into Bt-1 and Bt-2 fractions by the acid wash method (Procedure A—see the Experimental section), and ^{1}H and ^{13}C NMR spectra were recorded for each fraction. Each fraction contained three components which were readily distinguished in the ^{1}H NMR spectrum by the multiplicity of the methyl signals and the hydrogen(s) α- to the Bt group (see Tables 8 and 9 in the supplementary material for NMR spectral data).

With 10 mol% toluene-*p*-sulfonic acid, oct-1-ene and dec-1-ene each provided a simple binary mixture of the corresponding 2-(benzotriazol-1- and -2-yl)alkanes in *ca.* 45% yield (see Tables 4 and 5), which could be readily identified by examination of their ^{1}H NMR spectra (see Tables 10–13 in supplementary material). When one equivalent of toluene-*p*-sulfonic acid was used, the expected complex mixtures resulted (*ca.* 55% yields), although in these cases no rearrangement of the carbon skeleton was detected. Following the separation of these mixtures into

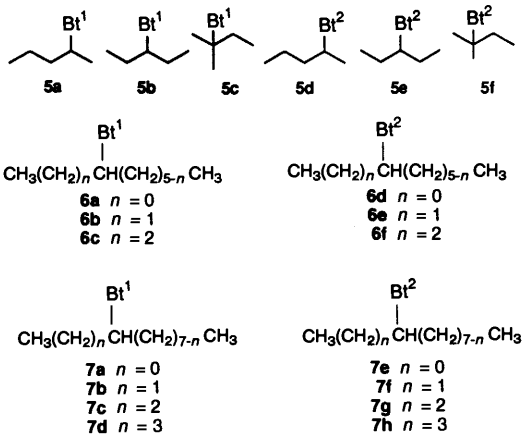

Fig. 3 Products of the addition of benzotriazole to *n*-alkenes

Table 4 Properties of isomeric benzotriazolyloctanes

Product[a]	t_R/min	Yield (%)[b,c] 10[d]	100[d]
Mixture of **6a–6c**	—	24.9	30.0
2-(Benzotriazol-1-yl)octane **6a**	20.88	(24.9)	(13.2)
3-(Benzotriazol-1-yl)octane **6b**	20.27	(0)	(10.4)
4-(Benzotriazol-1-yl)octane **6c**	20.03	(0)	(6.4)
Mixture of **6d–6f**	—	19.6	28.3
2-(Benzotriazol-2-yl)octane **6d**	18.96	(19.6)	(12.6)
3-(Benzotriazol-2-yl)octane **6e**	18.41	(0)	(9.5)
4-(Benzotriazol-2-yl)octane **6f**	18.18	(0)	(6.2)

[a] Satisfactory GC–HRMS data obtained for each isomer, *e.g.*, **6a** (Found: M^+, 231.1736. $C_{14}H_{21}N_3$ requires for *M*, 231.1735). [b] Isolated yields, GC yields in parentheses. [c] Note added in proof: in subsequent work, significantly lower yields of addition products were recovered for no apparent change in conditions. [d] mol% toluene-*p*-sulfonic acid used.

Table 5 Properties of isomeric benzotriazolyldecanes

Product[a]	t_R/min	Yield (%)[b] 10[c]	100[c]
Mixture of **7a–7d**	—	28.7	32.9
2-(Benzotriazol-1-yl)decane **7a**	23.2	(28.7)	(18.5)
3-(Benzotriazol-1-yl)decane **7b**	22.4	(0)	(8.7)
4-(Benzotriazol-1-yl)decane **7c**	22.0	(0)	(3.6)
5-(Benzotriazol-1-yl)decane **7d**	21.9	(0)	(2.1)
Mixture of **7e–7h**	—	17.4	20.8
2-(Benzotriazol-2-yl)decane **7e**	21.1	(17.4)	(10.9)
3-(Benzotriazol-2-yl)decane **7f**	20.5	(0)	(5.7)
4-(Benzotriazol-2-yl)decane **7g**	20.2	(0)	(2.5)
5-(Benzotriazol-2-yl)decane **7h**	20.1	(0)	(1.7)

[a] Satisfactory GC–HRMS data obtained for each isomer, *e.g.*, **7a** (Found: M^+, 259.2014. $C_{14}H_{21}N_3$ requires for *M*, 259.2048). [b] Isolated yields, GC yields in parentheses. [c] mol% toluene-*p*-sulfonic acid used.

Bt-1 and Bt-2 fractions by the acid wash method, further separation was carried out by preparative GC. In the octyl system, compound **6a** was separated from **6b** + **6c**, and **6d** was separated from **6e** + **6f** by this method. Based upon signal intensities (*ca.* 2:1), two sets of NMR spectra could be readily distinguished for the **6b** + **6c** mixture and also for the **6e** + **6f** mixture, but the individual spectra were very similar, and the components could not be identified by NMR. However, analysis of the isomer pairs by GC–MS did allow the identification of each structure. The MS cracking pattern for **6c** showed a characteristic loss of propyl and butyl fragments, while that of **6b** showed loss of ethyl and pentyl fragments. (The MS cracking patterns for these compounds have been examined in detail using high-resolution MS techniques and will be fully discussed in a separate paper.)[8] The **6e–6f** pair could be similarly distinguished. Although NMR data could not be used to assign these structures, the correct structure could be unambiguously assigned to the appropriate NMR sub-spectrum based upon signal intensities (2:1) (see Tables 10 and 11 in the supplementary material). In the decyl system **7a**, **7b**, **7e** and **7f** were each isolated using preparative GC, but binary mixtures of **7c** + **7d** and **7g** + **7h** were obtained. These pairs of isomers were identified in the same manner as for the octyl system (see Tables 12 and 13 in the supplementary material).

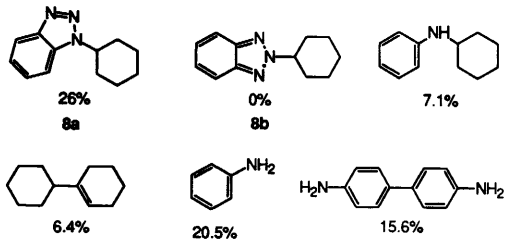

Fig. 4 Products from the reaction of benzotriazole with cyclohexene and TsOH at 180 °C

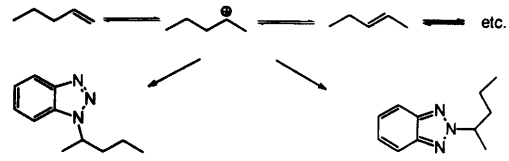

Fig. 5 Mechanism of BtH addition to alkenes

Addition of BtH to cyclohexene

At 120 °C cyclohexene gave 1-cyclohexylbenzotriazole **8a** (52%) and 2-cyclohexylbenzotriazole **8b** (47%) (isolated yields): it was completely unreactive toward BtH at 80 °C, while at 180 °C a complex mixture was formed which contained 26% of the expected product (see Fig. 4).

Discussion

The additions of BtH to terminal alkenes catalysed by 10 mol% of toluene-*p*-sulfonic acid lead regiospecifically (as monitored by GC) to the isolation in moderate to good yields of binary mixtures of the corresponding 2-(benzotriazol-1- and -2-yl)-alkanes. These products arise from initial protonation of the starting alkene followed by quenching of the intermediate cation with benzotriazole, either at N-1 or N-2. Terminal substitution by Bt was neither observed nor expected since this would require the intermediacy of an unfavourable primary cation. At the 10 mol% catalyst level, rearrangement of the starting alkene was observed only in the case of allylbenzene which is highly susceptible to acid-catalysed rearrangement.[9]

When these reactions were carried out in the presence of 1 molar equivalent of toluene-*p*-sulfonic acid, complex mixtures resulted. The composition of these mixtures are well explained by acid-catalysed isomerization of the starting alkenes into a mixture containing all alkenes of the same carbon skeleton, and subsequent reaction of benzotriazole with the series of intermediate carbocations thus formed (see Fig. 5). Double

bond isomerization in *n*-alkenes is known to be facile under acidic conditions.[9]

The predominant addition product was usually substituted with Bt at position 2 on the alkyl chain, with progressively smaller amounts of substitution at positions further removed. This distribution is related to the relative stability of the intermediate carbocation (2° more stable than 1°, precluding terminal substitution) in the double bond migration, and the number of consecutive isomerizations needed to propagate the double bond along the chain. When pure 2-(benzotriazol-1-yl)octane was treated with one equivalent of toluene-*p*-sulfonic acid under the standard reaction conditions no rearrangement was observed, even when the temperature was raised high enough to cause decomposition. Thus, rearrangement occurs only in the starting alkene.

In the phenylalkene series, the distribution was affected by the fact that the phenyl group could stabilize and effectively 'trap' the carbocation at the position furthest removed from the original double bond, increasing the proportion of the isomer with benzotriazole substituted α to the phenyl. In the reaction of 4-phenylbut-1-ene with BtH, GC–MS analysis of the residual alkene showed a mixture of three isomers in the ratio 10:30:60, compared with the three regioisomeric addition products in the ratio of 12:20:68. This distribution of double bond migrations was consistent with literature studies,[9] and is shown to match closely the distribution of benzotriazole substitution along the chain.

In most experiments there were roughly equal amounts of the Bt-1 and Bt-2 substituted compounds formed, however, the amount of 2-benzotriazolylalkanes formed varied considerably in some cases.

Conclusions

The acid-catalysed addition of benzotriazole to unactivated alkenes represents a simple and direct approach to the preparation of a wide variety of benzotriazol-1- and -2-ylalkanes in moderate to good yields. These reactions constitute the first examples of NH nucleophile addition to unactivated double bonds at moderate temperatures and pressures.

Experimental

General

Melting points were measured on a hot-stage microscope and are uncorrected. ^{1}H and ^{13}C NMR data were recorded at either 300 MHz and 75 MHz respectively, or 500 MHz and 125 MHz respectively, with Me_4Si (δ = 0.00) as the internal reference in deuteriochloroform or deuteriated DMSO, as indicated. All GC retention times were determined on an HP5890 Series II Capillary GC operating in split mode with helium as the carrier gas and fitted with a mass selective detector (MSD). The mass spectra recorded for each compound synthesized are in agreement with the proposed structures, and will be published separately.[8] The column used was an HP5 capillary column 30 m × 0.25 mm, with 0.25 μm film thickness of 5% phenyl methyl silicone gum. The temperature program used an initial temperature of 50 °C for 1 min, then ramped at 10 °C min^{-1} to 250 °C. The GC yield was determined from the integration of the total ion current from the MSD. The preparative GC separations were carried out on a GM 580 Isothermal GC fitted with a $\frac{1}{4}$ in. stainless steel column packed with 10% OV-101 on Chromosorb W-HP with helium carrier gas using a thermal conductivity detector. Preparative GC runs were carried out isothermally at 145 to 180 °C, and separations were achieved on the basis of boiling point with compounds eluting from the packed column in the same order as on the capillary column specified above. All starting materials were supplied by Aldrich or Fisher and used without further purification. Satisfactory ^{1}H and ^{13}C NMR spectra were recorded for all starting materials.

General procedures A and B: 10 mol% toluene-*p*-sulfonic acid

Benzotriazole (1.19 g, 10 mmol), toluene-*p*-sulfonic acid (procedure A: 0.18 g, 1 mmol; procedure B: 1.8 g, 10 mmol) and alkene (15 mmol) were heated in a sealed tube at 80 °C. After 12–20 h the sticky residue was dissolved in ethyl acetate (50 cm^3), and washed with 10% NaOH (3 × 25 cm^3). After drying over $MgSO_4$ the solvent was removed and the residue purified by crystallization if possible. The Bt-1 and Bt-2 substituted isomers were separated by stirring the mixture in concentrated hydrochloric acid (30 cm^3) for 3 h, and extracting with ether (3 × 10 cm^3), to provide the Bt-2 compounds. On dilution with water, and extraction with ether, the Bt-1 isomers were recovered.

BtH and styrene. The addition reaction was carried out according to procedure A for 12 h, and the resulting mixture was separated by column chromatography (silica gel; 5:5:1 chloroform–*n*-hexane–ethanol) to give a 46% combined yield of 1-(*benzotriazol-1-yl*)-1-*phenylethane* **2a** and 1-(*benzotriazol-2-yl*)-1-*phenylethane* **2b** in the ratio of 6.5:1 (see Table 1). When the reaction was carried out according to procedure B, the same compounds were produced in 50% yield, in the ratio 2:1 (see Tables 1, 6 and 7).

BtH and allylbenzene. The reaction was carried out using procedure A for 14 h to yield 1.71 g (66%) of a mixture of four pure isomers, which were partially separated by acid washing (*cf.*, procedure A). The two components of the Bt-1 fraction were separated by crystallization from ether to give colourless needles of 1-(*benzotriazol-1-yl*)-1-*phenylpropane* **3a** (440 mg, 18%), mp 123 °C, and a yellow oil, 2-(*benzotriazol-1-yl*)-1-*phenylpropane* **3b** (550 mg, 23%). The Bt-2 fraction (550 mg, 23%) consisted of 1-(*benzotriazol-2-yl*)-1-*phenylpropane* **3c** and 2-(*benzotriazol-2-yl*)-1-*phenylpropane* **3d** (13.3% and 10.6% yield, respectively, as determined by NMR spectroscopy). When the reaction was carried out using procedure B, 1.87 g (72%) of a mixture of **3a**, **3b**, **3c** and **3d** was obtained (see Tables 1, 6 and 7).

BtH and 4-phenylbut-1-ene. Under the conditions of procedure A, 4-phenylbut-1-ene produced 1.6 g (65%) of a mixture of two isomers. One component of the mixture, 3-(*benzotriazol-2-yl*)-1-*phenylbutane* **4f**, was isolated by flash chromatography (silica; eluent 6:5 chloroform–*n*-pentane) as a light yellow oil (25%): δ_H(300 MHz; $CDCl_3$) 7.88 (2 H, dd, *J* 2.0 and 2.8), 7.35 (2 H, dd, *J* 2.0 and 2.8), 7.30–7.10 (5 H, m), 5.1–4.9 (1 H, m), 2.70–2.40 (3 H, m), 2.30–2.10 (1 H, m) and 1.72 (3 H, d, *J* 7.3); δ_C(75 MHz; $CDCl_3$) 144.1, 140.8, 128.4, 126.1, 118.1, 62.7 (CH), 38.5, 32.3 and 21.3 (CH_3); *m/z* (70 eV) 251 (M^+, 17%), 222 (6, $M^+ - 29$), 118 (19, $C_6H_4N_3^+$), 105 (15) and 91 (100). The other component was identified by GC–MS to be 3-(*benzotriazol-1-yl*)-1-*phenylbutane* **4c**. When procedure B was employed, 1.5 g (61%) of a mixture of six isomers was produced, and these isomers were identified by GC–MS (see Table 2).

BtH and *n*-pentene. Following procedure A, pentene produced a mixture of 2-(*benzotriazol-1-yl*)*pentane* **5a**, 3-(*benzotriazol-1-yl*)*pentane* **5b**, and 2-(*benzotriazol-2-yl*)*pentane* **5d** in 27% overall yield. Using procedure B, a mixture of six isomers was produced in 38% combined yield. The mixture was separated into Bt-1 and Bt-2 fractions by the acid washing method, and the components identified on the basis of their ^{1}H and ^{13}C NMR and GC–MS data (see Tables, 3, 8 and 9).

BtH and *n*-octene. Following procedure A, octene produced a mixture of 2-(*benzotriazol-1-yl*)*octane* **6a** and 2-(*benzotriazol-2-yl*)*octane* **6d** in 45% overall yield. When procedure B was used a mixture of six isomers was produced in 58% yield. The mixture

was separated into Bt-1 and Bt-2 fractions by acid washing, and these fractions were further separated by preparative GC. Compounds **6a** and **6d** were obtained pure, while **6b** + **6c** and **6e** + **6f** were obtained as binary mixtures. Compounds were identified on the basis of their ^{1}H and ^{13}C NMR, and GC–MS (see Tables 4, 10 and 11).

BtH and *n*-decene. Using method A, decene produced a mixture of 2-(benzotriazol-1-yl)decane **7a** and 2-(benzotriazol-2-yl)decane **7e** in 46% overall yield. When procedure B was employed a mixture of eight isomers was produced in 54% yield. The mixture was separated into Bt-1 and Bt-2 fractions by acid washing, and these fractions were further separated by preparative GC. Compounds **7a**, **7b**, **7e** and **7f** were obtained pure, while **7c** + **7d** and **7g** + **7h** were obtained as pure mixtures. Compounds were identified on the basis of their ^{1}H and ^{13}C NMR, and GC–MS (see Tables 5, 12 and 13).

BtH and cyclohexene. The reaction was carried out for 15 h at 120 °C according to procedure B to give a mixture of two isomers. The mixture was separated by crystallization from ether to give the following two products: 1-benzotriazol-1-ylcyclohexane **8a**. Yield 0.59 g (29%), colourless crystals, mp 104 °C (lit.,[10] 102 °C); δ_H(300 MHz; $CDCl_3$) 8.05 (1 H, d, *J* 7.3), 7.58 (1 H, d, *J* 7.3), 7.45 (1 H, t, *J* 4.9), 7.36 (1 H, t, *J* 4.9), 4.72–4.60 (1 H, m), 2.22–2.10 (4 H, m), 2.05–1.90 (2 H, m), 1.85–1.75 (1 H, m) and 1.60–1.30 (3 H, m); δ_C(75 MHz; $CDCl_3$) 146.06, 132.20, 126.66, 123.58, 120.03, 109.70, 59.01, 32.53, 25.57 and 25.26; *m/z* (70 eV) 201 (M^+, 100%), 172 (26, $M^+ - 29$), 158 (40, $M^+ - 43$), 119 (30, $C_6H_5N_3^+$), 118 (28, $C_6H_4N_3^+$), 117 (27, $C_6H_3N_3^+$) and 91 (95). Benzotriazol-2-ylcyclohexane **8b**. Yield 0.54 g (27%); δ_H(300 MHz; $CDCl_3$) 7.85 (2 H, dd, *J* 2 and 3.2), 7.35 (2 H, dd, *J* 2 and 3.2), 4.85–4.70 (1 H, m), 2.40–2.25 (3 H, m), 2.20–1.90 (4 H, m), 1.85–1.65 (1 H, m) and 1.60–1.30 (2 H, m); δ_C(75 MHz; $CDCl_3$) 143.87, 125.88, 117.94, 65.90, 33.10, 25.21 and 25.13; *m/z* (70 eV), 201 (M^+, 45%), 120 (100, $C_6H_6N_3^+$), 119 (31, $C_6H_5N_3^+$) and 91 (39).

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