The Chemistry of *N*-Substituted Benzotriazoles. Part 2.[1] Reactions of Benzotriazole with Aldehydes and Aldehyde Derivatives. 1-(α-Hydroxyalkyl)-, 1-(α-Alkoxyalkyl)-, and 1-(α-Acyloxyalkyl)benzotriazoles

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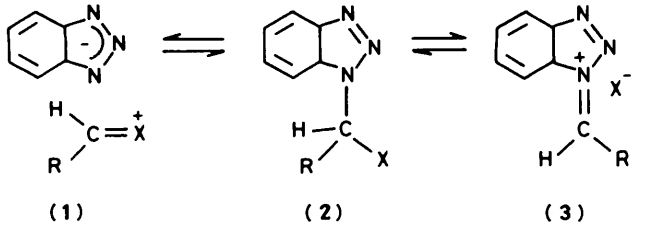
Benzotriazole reacts readily with a variety of aldehydes to yield crystalline 1 : 1 adducts characterized by strong hydrogen bonding. Corresponding 1-(α-alkoxyalkyl)benzotriazoles are formed in the presence of alcohols, and 1-(α-acetoxyalkyl) analogues result from aldehyde diacetoxy derivatives. The products of more complex reactions between benzotriazoles and unsaturated aldehydes are elucidated.

Our investigation of 1-(chloromethyl)benzotriazole[1] demonstrated that benzotriazole is an excellent *N*-heterocyclic system for the stabilization of the *N*–CH_2–Cl group probably because it increases the importance of the covalent form (**2**) over that of the ionic form (**3**) (Scheme 1). This property is caused by the strong electron withdrawing ability of the –N=N– grouping, which is also reflected in the acidity of benzotriazole (pK_a 8.2),[2] comparable with that of uracil (9.45)[3] or phenol (9.97)[4] rather than with pyrrole (23)[5] or carbazole (19.9).[5] Benzimidazole (pK_a 13.2)[6] gives a stable 1-chloromethyl derivative[7,8] only after protonation at N-3, which enhances the electron withdrawing properties of the system dramatically. Other compounds of type RR^1NCH_2X, derived from less acidic RR^1NH parents, undergo spontaneous ionization to iminium ions $RR^1\overset{+}{N}{=}CH_2$ [analogues of (**3**)], when X represents a good leaving group. Because of the reactivity of iminium ions $RR^1\overset{+}{N}{=}CH_2$, such processes often lead to rapid conversion.



(1) (2) (3)

Scheme 1.

Conversely, strong electron withdrawal by the benzotriazole system destabilizes the N–C bond of (**2**), allowing dissociation to give (**1**), especially when X is a strong electron donor group such as dimethylamino.[9] This property is of potential use in chemical synthesis. A benzotriazole moiety can be used as an anchor and as an activator of neighbouring bonds to construct a new molecular assembly followed by cleaving of the C–N bond to release a new molecule. The susceptibility of the system towards cleavage can be enhanced by quaternization at the 3-position of the benzotriazole.[1]

We now extend the previous work,[1] to compounds of type (**2**; R = H), to new reactions, and to various substituents. We discuss the stability and reactivity of (**2**), where X is a hydroxy, alkoxy, or acyloxy group and when R is hydrogen, alkyl, or aryl, in respect to their instrinsic reactivity and to their potential further use in organic synthesis.

Hydroxyalkylation of Benzotriazole.—The well known[10] reaction of benzotriazole with formaldehyde gives benzotriazolylmethanol (**6a**), a useful starting material which is transformed into 1-(chloromethyl)benzotriazole by thionyl chloride.[10] Only four other aldehydes † have previously been condensed with benzotriazole in a manner similar to formaldehyde: *m*- and *p*-nitrobenzaldehyde,[11] chloral,[12] and *o*-vanillin.[13]

We now find the reaction is general, at least for aliphatic aldehydes. Benzotriazole and the appropriate aliphatic aldehyde react with evolution of heat, and used in exactly 1 : 1 proportions, soon solidified to give the novel 1 : 1 benzotriazole–aldehyde adducts (**6b—i**) (Table 1) which could be recrystallized from dry diethyl ether. Addition of a small amount of the aldehyde to the recrystallized solvent prevents co-precipitation of benzotriazole along with the adduct. The products after drying at room temperature under reduced pressure could be stored in capped vials for months without any decomposition.

I.r. spectra of the products lack carbonyl absorption and reveal a strong band at 3 100—3 200 cm^{-1} originating from a strongly hydrogen bonded OH group. The O–H stretching vibrations shift is a measure of the energy of hydrogen bonding,[14] and indicates strengths of the OH • • • N bonding to fall between that of alcohol–pyridine and phenol–pyridine pairs.

N.m.r. spectra of the adducts showed that there is an equilibrium between starting materials and 1-benzotriazol-1-ylalkanol (**6**) in solution (Scheme 2). The equilibrium position can be determined by comparison of the intensities of the characteristic adduct signals from the protons at the α-carbon (at 6.5 p.p.m.) with those of the starting aldehydes (at 10 p.p.m.) which do not overlap with other signals. The proportions of product and starting materials depend strongly on the concentration of the solution and for the butyraldehyde adduct in chloroform change from about 5 : 1 for a 50% solution to 2 : 1 when the concentration is decreased to 10%. The equilibrium constant depends also on the nature of the solvent used (higher in carbon tetrachloride and in dimethyl sulphoxide than in chloroform) and on the aldehyde. The comparatively low stability of the product derived from trimethylacetaldehyde is probably caused by steric hindrance. Bases (*e.g.* triethylamine) or acids (*e.g.* trifluoroacetic acid) shift the equilibrium strongly towards the starting materials.

No reaction was observed when benzaldehyde or *p*-tolualdehyde were mixed with benzotriazole but 4-pyridinecarbaldehyde reacted with evolution of heat and the crystalline product (**6j**) (Table 1) was soon precipitated. Surprisingly, strong hydrogen bonding in adduct (**6j**) (i.r. band at 2 600 cm^{-1}), comparable with that between pyridine and acetic acid,[15] requires further investigation.

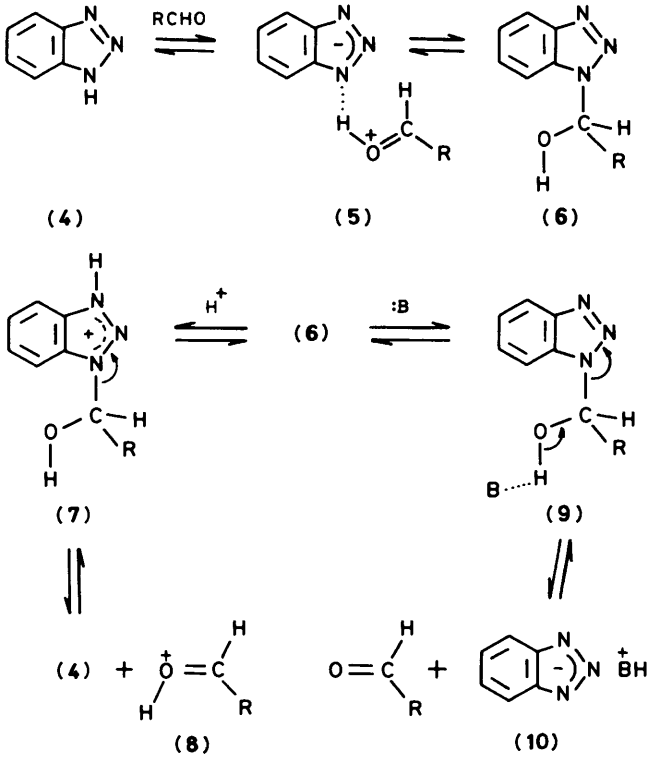
A reaction mechanism consistent with these observations starts by nucleophilic attack of benzotriazole (or its anion) on a protonated carbonyl groups (Scheme 2). When product (**6**) is of low solubility in the solvent used, it is precipitated, and this

† See footnote on p. 796.

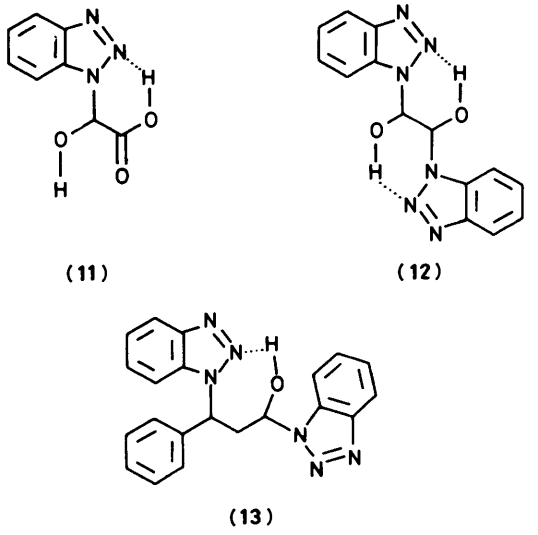
Table 1. 1-(1-Hydroxyalkyl)benzotriazoles (**6**)[a]

Product No.	R	Formula	M.p. (°C) (decomp.)	Found (%) (Required) C	H	N	$\nu_{max.}$(OH)[b] (cm^{-1})	δ(CH–O) (p.p.m.) (*J*/Hz)
(**6a**)	H	$C_7H_7N_3O$	135—137[c]	56.5 (56.4)	4.7 (4.7)	28.2 (28.2)	3 182	6.12 (s)[d]
(**6b**)	Me	$C_8H_9N_3O$	74—75	58.8 (58.9)	5.6 (5.6)	25.7 (25.8)	3 140	6.55 (q, *J* 6.3)
(**6c**)	Et	$C_9H_{11}N_3O$	63—65	60.9 (61.0)	6.2 (6.3)	23.9 (23.7)	3 148	6.54 (t, *J* 7.0)
(**6d**)	Pr	$C_{10}H_{13}N_3O$	61—63	62.6 (62.8)	6.9 (6.9)	22.3 (22.0)	3 162	6.61 (t, *J* 6.8)
(**6e**)	Pr^i	$C_{10}H_{13}N_3O$	58—61	62.6 (62.8)	6.8 (6.9)	22.4 (22.0)	3 187	6.25 (d, *J* 8.6)
(**6f**)	Bu	$C_{11}H_{15}N_3O$	40—41	64.2 (64.4)	7.3 (7.4)	20.7 (20.5)	3 184	6.61 (t, *J* 6.9)
(**6g**)	Bu^t	$C_{11}H_{15}N_3O$	54—56	64.1 (64.4)	7.2 (7.4)	20.7 (20.5)	3 189	6.48 (s)
(**6h**)	$(CH_2)_5Me$	$C_{13}H_{19}N_3O$	53—54	66.6 (66.9)	8.3 (8.2)	18.8 (18.0)	3 183	6.62 (t, *J* 6.8)
(**6i**)	$(CH_2)_7Me$	$C_{15}H_{23}N_3O$	54—55	68.8 (68.9)	9.2 (8.9)	16.1 (16.1)	3 182	6.67 (t, *J* 7.0)
(**6j**)	4-Pyridyl	$C_{12}H_{10}N_4O$	103—104	63.8 (63.7)	4.5 (4.5)	24.4 (24.8)	2 589	7.5 < (s) < 8.3[e]

[a] All found in 100% yield. [b] Spectra taken for 50% $CHBr_3$ solutions or mulls. [c] Lit.,[10] m.p. 148—151 °C. [d] $CDCl_3$–[$^2H_6$]-DMSO (3:1) as a solvent. [e] The signal is overlapping with those of aromatic protons.



Scheme 2.



shifts the equilibrium to the right. Protonation of the N-3 nitrogen atom (**7**) or O–H proton abstraction by a base (**9**) decomposes (**6**) to the starting materials. In the absence of added compounds, molecules of (**6**) may serve themselves as proton donors and proton acceptors in the degradation pathways. If R is electron withdrawing, this stabilizes the bond with N-1 of benzotriazole protecting (**7**) and (**9**) against cleavage.

Structural features which allow strong intramolecular hydrogen bonding between OH and N-2 provide such α-hydroxyalkylbenzotriazoles with considerable stabilization. Thus, product (**12**) was obtained in high yield. Adduct (**13**)[16] was formed when benzotriazole and cinnamaldehyde were heated neat but it partially dissociated to starting materials in water or methanol, whereas compounds (**11**) and (**12**) can be heated in water without decomposition. The difference in stability of these compounds could reflect the different stability on the six-membered hydrogen bonded rings of (**11**) and (**12**) compared to the seven-membered ring of (**13**).

Alkoxyalkylation of Benzotriazole.—Although the acid-catalysed reaction of heterocyclic amines with aliphatic aldehydes and alcohols leading to α-alkoxyalkyl derivatives is well established for carbazole,[17,18] only two examples have previously been described for benzotriazole:[18] those with acetaldehyde and with propionaldehyde (in each case with ethanol as the alcohol).

Other previously described 1-(1-alkoxyalkyl)benzotriazoles

Table 2. 1-(1-Alkoxyalkyl)benzotriazoles (**16**)

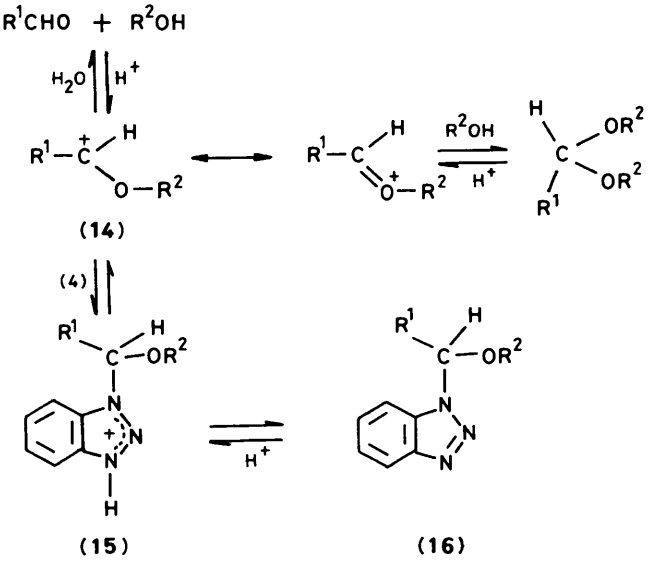
Product No.	R^1	R^2	Formula	Yield (%)	M.p. (°C)	Found (%) (Required) C	H	N	High-res. m.s. Found (Calc.)	δ(N–CH–O) (p.p.m.) (*J*/Hz)
(**16a**)	H	Me	$C_8H_9N_3O$	20	Oil[a]				163.0735 (163.0745)	6.11 (s)
(**16b**)	Me	Me	$C_9H_{11}N_3O$	75	Oil	61.1 (61.0)	6.3 (6.3)	23.7 (23.7)		6.23 (q, *J* 6.4)
(**16c**)	Pr^i	Me	$C_{11}H_{15}N_3O$	99	Oil				205.1215 (205.1215)	5.60 (d, *J* 8.8)
(**16d**)	Bu^t	Me	$C_{12}H_{17}N_3O$	54	86—87	65.7 (65.7)	8.0 (7.8)	19.2 (19.2)		5.71 (s)
(**16e**)	Pr^i	Pr^i	$C_{13}H_{19}N_3O$	96	64—65				233.1530 (233.1528)	5.81 (d, *J* 8.8)
(**16f**)	Ph	Me	$C_{14}H_{13}N_3O$	91	Oil[b]	70.1 (70.3)	5.5 (5.5)	17.5 (17.6)		7.14 (s)
(**16g**)	Pr^i	Bu^t	$C_{14}H_{21}N_3O$	98	80—82	67.7 (68.0)	8.9 (8.6)	17.0 (17.0)		6.05 (d, *J* 8.8)
(**16h**)	Bu^t	Pr^i	$C_{14}H_{21}N_3O$	82	130—131	68.3 (68.0)	8.9 (8.6)	17.2 (17.0)		5.90 (s)
(**16i**)	C_6H_4Me-*p*	Me	$C_{15}H_{15}N_3O$	64	Oil	71.0 (71.1)	6.0 (6.0)	16.5 (16.6)		7.20 (s)
(**16j**)	Pr^i	Cyclohexyl	$C_{16}H_{23}N_3O$	98	Oil	70.3 (70.4)	8.9 (8.5)	15.4 (15.4)		6.00 (d, *J* 9.0)
(**16k**)	Bu^t	CH_2Bu^t	$C_{16}H_{25}N_3O$	90	65—68	69.7 (69.8)	9.4 (9.2)	15.2 (15.3)		8.3 (s)

[a] Previously obtained as an oil from benzotriazole and methoxymethyl chloride.[19] [b] Previously obtained as an oil (13%) from 1-chlorobenzotriazole and methylbenzyl ether.[23]

were obtained by more complicated methods. Thus, 1-methoxymethylbenzotriazole,[19] was prepared by reaction of benzotriazole with methoxymethyl chloride. Several such derivatives of benzotriazole, derived mainly from long aliphatic chain aldehydes or similar alcohols were obtained by an addition of benzotriazole to appropriate vinyl ethers and were used as components for lubricating oils.[20] 1-Tetrahydropyran-2-ylbenzotriazole[21] was obtained in a similar manner from dihydropyran. Reaction of 1-chlorobenzotriazole with (saturated) ethers also affords 1-alkoxyalkylbenzotriazoles, although in low yields: 1-(1-ethoxyethyl)-,[22,23] 1-tetrahydrofuran-2-yl-,[22,23] 1-(1-methoxybutyl)-,[23] 1-(1,4-dioxan-2-yl)-,[23] and methoxybenzylbenzotriazole.[23]

Compounds with the group $-CHR^1-O-R^2$ linked to a heterocyclic nitrogen atom—nucleosides (in which R^1 and R^2 are part of a sugar residue) or nucleoside analogues (in which R^1 = H or alkyl and R^2 = alkyl)—are of great importance for biochemistry.[24–30] Synthesis of many nucleosides derived from benzotriazole and D-ribofuranose,[31–35] (D-glucopyranose,[34,36–42] D-xylopyranose,[38,41] D-galactose,[39,43] or other sugars[42,44,45]) has been reported, usually by reaction of glycosyl halides with trialkylsilylbenzotriazoles or benzotriazole salts. Some possess antitumor activity.[34,37,38,46–48] Much recent interest[49–58] in nucleoside analogues derived from other heterocyclic systems derives from their anti-herpes viral activity.

We now show that such compounds can be derived quite generally from benzotriazole and aliphatic aldehydes and that aromatic aldehydes can also be used (Scheme 3). The reaction proceeds smoothly under simple conditions and gives products (**16b—i**) in high yields (Table 2). Sometimes the crude products gave correct analyses without further purification. The best work-up is ether extraction of the products from aqueous sodium carbonate in which benzotriazole is soluble and is thus simply removed from the reaction mixture. Any excess of volatile aldehyde was removed by evaporation under reduced pressure.



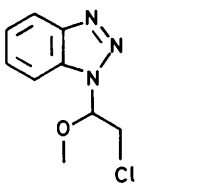
Scheme 3.

The reaction involves electrophilic attack of the alkoxyalkyl carbonium ion (**14**) on N-3 of the benzotriazole system to produce the more stable ion (**15**) which on deprotonation gives the product (**16**) (Scheme 3). Initial reaction of the aldehyde at the NH group followed by substitution of the hydroxy group by alkoxy (as suggested for the case of carbazole[15]) seems less probable because of the tendency of 1-benzotriazolyl-1-alkanols to cleave the N–C bond in acidic solution. Reaction of aldehydes with alcohols[59,60] is fast under the conditions used and the concentration of alkoxyalkyl carbonium ions (as potential nucleophiles) is probably higher than that of their hydroxyalkyl analogues.

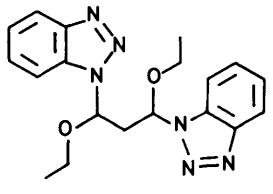
The same alkoxyalkyl carbonium ions are intermediates

when acetals are used as starting materials (Scheme 3). The reaction is also fast and smooth and is especially valuable for the preparation of products such as (**17**) and (**18**) derived from unstable aldehydes such as chloroacetaldehyde or malonaldehyde. Alkoxyalkylation of heterocyclic NH groups by this method was reported previously for pyrazole,[61] carbazole,[62] and purine.[63]

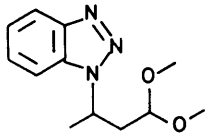
Reactions of benzotriazole with unsaturated aldehydes and alcohols are more complicated. From complex reaction mixtures, the products (**19**) and (**20**) of addition of benzotriazole to double bonds followed by acetalization of carbonyl groups were isolated from reactions of crotonaldehyde with benzotriazole and methanol or ethanol, respectively.



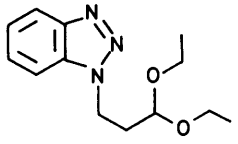
(**17**)



(**18**)

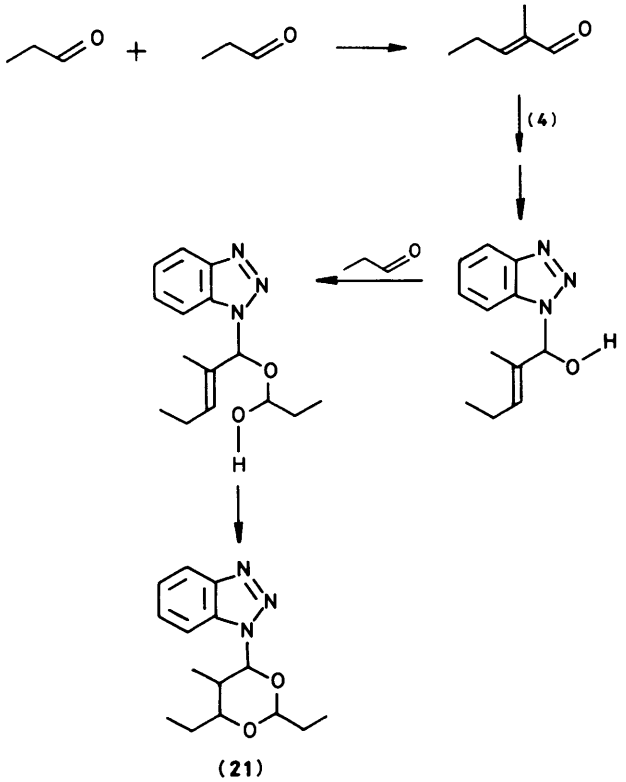


(**19**)



(**20**)

Compound (**21**) with alkoxyalkyl character was obtained when benzotriazole was heated with propionaldehyde in acetic acid solution with catalytic amounts of sulphuric acid at 80 °C for 3 h. The probable reaction sequence is shown in Scheme 4.



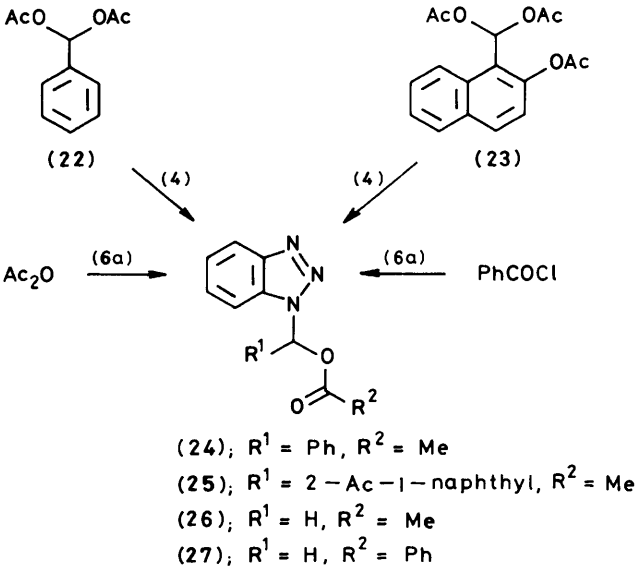
(**21**)

Scheme 4.

The structure of (**21**) is supported by the n.m.r. spectrum: two different ethyl groups (triplets: at 0.84 and 1.00 p.p.m.), one methyl group coupled with only one proton (doublet at 1.37 p.p.m.) and one proton on the carbon α to the benzotriazole system (singlet at 6.14 p.p.m.). That this last signal is not split indicates that it and its neighbour occupy different positions on the six-membered ring (axial-equatorial or equatorial-axial). A slightly broadened quartet at 3.12 p.p.m. from the β–CH shows only weak coupling with the γ–CH. Hence all substituents on the ring are equatorial, except the methyl which is axial. Therefore, compound (**21**) must be the *cis-cis-cis* isomer.

Acyloxyalkylbenzotriazoles.—Direct acyloxyalkylation of benzotriazole is achieved using aldehyde diacyloxy derivatives. Thus, 1-(α-acetoxybenzyl)benzotriazole (**24**) was obtained from α,α-diacetoxytoluene (**22**) by a similar procedure to that used with diacetals. The reaction mechanism is probably also similar to that given for diacetals in Scheme 3, involving an attack of the appropriate carbonium ion on N-3 of the benzotriazole system. The triacetoxy derivative of 2-hydroxynaphthalene-1-carbaldehyde (**23**) gave compound (**25**) on being heated with benzotriazole at 125 °C (Scheme 5).

Starting from 1-hydroxymethylbenzotriazole, the acyloxy derivatives (**26**) and (**27**) were obtained in good yields using acetic anhydride or benzoyl chloride with 4-dimethylaminopyridine (DMAP).



(**24**); R^1 = Ph, R^2 = Me
(**25**); R^1 = 2–Ac–1–naphthyl, R^2 = Me
(**26**); R^1 = H, R^2 = Me
(**27**); R^1 = H, R^2 = Ph

Scheme 5.

Experimental

M.p.s were determined on a Bristoline hot-stage microscope and are uncorrected. I.r. spectra were recorded with a Perkin-Elmer 283B grating spectrophotometer as thin films (liquids) or as bromoform solutions or mulls (solids). ^{1}H N.m.r. spectra were recorded on a Varian EM 360L (60 MHz) instrument for solutions in deuteriochloroform (tetramethylsilane as internal reference) unless otherwise stated. Low and high resolution mass spectra were determined at 70 eV with an A.E.I. MS–30 mass spectrometer operating with a Kratos DS–55 data system. Column chromatography was performed using M.C.B. Silica Gel (230—400 mesh) and a slight positive pressure.

1-(1-*Hydroxyethyl*)*benzotriazole* (**6b**).—Benzotriazole (0.59 g, 5 mmol) and acetaldehyde (1.12 ml, 20 mmol) were dissolved in boiling diethyl ether. The solution was filtered and kept for 12 h at 25 °C to give *benzotriazole–acetaldehyde* (1:1) adduct (**6b**)

(0.52 g, 64%) as needles which were washed with pentane and dried *in vacuo* at 25 °C (Table 1). Additional (**6b**) (0.27 g, 33%) was obtained by dilution of the filtrate with pentane and cooling to −5 °C.

1-(1-*Hydroxyalkyl*)*benzotriazoles* (**6c—i**): *General Procedure.*—Benzotriazole (1.19 g, 10 mmol) was dissolved in the aldehyde (10 mmol) by gentle warming, and then kept at 25 °C. The liquid solidified in times varying from minutes, *e.g.* (**6e**), to days, (**6f**). The products were dissolved in diethyl ether containing 10% of the appropriate aldehyde, and the solutions were cooled slowly from 30 to −5 °C to give the crystalline product. Tetrahydrofuran (THF) was used for recrystallization of (**6e**) and (**6g**) because of their low solubility in diethyl ether. Analytical and spectral data of the products are given in Table 1.

Benzotriazol-1-*yl*-(4-*pyridyl*)*methanol* (**6j**).—Benzotriazole (2.38 g, 20 mmol) and 4-pyridinecarbaldehyde (2.39 ml, 25 mmol) were dissolved in THF. The product crystallized as prisms which were filtered off, washed with diethyl ether, and dried *in vacuo* at 25 °C to give the alcohol (**6j**) (3.79 g, 84%). Analytical and spectral data are given in Table 1.

Benzotriazol-1-*yl*(*hydroxy*)*acetic Acid* (**11**).—Benzotriazole (5.96 g, 50 mmol) was dissolved in acetic acid (15 ml) at 70 °C. Sulphuric acid (2 drops) followed by 50% aqueous glyoxalic acid (5.52 ml, 50 mmol) was added. The mixture was heated at 80 °C for 30 min and kept at 25 °C for 12 h. The mixture was cooled for 24 h at 0 °C after which the product was filtered off, washed with toluene (×3) and dried *in vacuo* to give white needles of the *acid* (**11**) (7.45 g, 78%), m.p. 136—137 °C, unchanged by recrystallization from toluene–dioxane (2:1) (Found: C, 49.6; H, 3.6; N, 21.7. $C_8H_7N_3O_3$ requires C, 49.7; H, 3.7; N, 21.8%); $\nu_{max.}$(Nujol) 3 433, 1 724, 1 275, 1 128, 1 101, 894, 746, and 709 cm^{-1}; δ($CDCl_3$–[$^2H_6$]-DMSO) 6.83 (1 H, s), 7.56 (2 H, m), 8.02 (2 H, m), and 9.02 (2 H, br s).

1,2-*Dibenzotriazol*-1-*ylethane*-1,2-*diol* (**12**).—Benzotriazole (5.96 g, 50 mmol), sulphuric acid (2 drops), and acetic acid (15 ml) were stirred at 75 °C, and glyoxal (40% aqueous solution; 3.63 g, 25 mmol) was added. Precipitation began immediately. The mixture was kept at 25 °C for 24 h, after which the solid was filtered off, washed with acetic acid, then water (×2) and dried at 60 °C/20 mmHg to give prisms of the diol (**12**) (7.40 g, 100%), m.p. 167—169 °C (Found: C, 56.6; H, 4.1; N, 28.3. $C_{14}H_{12}N_6O_2$ requires C, 56.8; H, 4.1; N, 28.4%); $\nu_{max.}$ 3 110, 1 278, 1 160, 1 075, 933, and 760 cm^{-1}; δ($CDCl_3$–[$^2H_6$]-DMSO, 2:1) 7.25—8.30 (m).

1,3-*Dibenzotriazol*-1-*yl*-3-*phenylpropan*-1-*ol* (**13**).—Benzotriazole (2.38 g, 20 mmol) and *trans*-cinnamaldehyde (1.32 g, 10 mmol) were heated under nitrogen at 120 °C for 4 h. The reaction mixture was cooled to 25 °C, triturated with diethyl ether (25 ml), and the resulting propanol (**13**) (2.07 g, 56%) recrystallized from toluene as prisms, m.p. 120—122 °C (Found: C, 67.8; H, 4.9; N, 23.1. $C_{21}H_{18}N_6O$ requires C, 68.1; H, 4.9; N, 22.7%); $\nu_{max.}$ 3 150, 1 451, 1 272, 1 104, 998, and 743 cm^{-1}; δ($CDCl_3$–[$^2H_6$]-DMSO, 2:1) 3.15—4.30 (2 H, m), 5.80—6.80 (2 H, m), and 7.15—8.30 (14 H, m).

1-(*Methoxymethyl*)*benzotriazole* (**16a**).—Benzotriazole (1.19 g, 10 mmol), dimethoxymethane (1.52 g, 20 mmol), sulphuric acid (1 drop), and benzene (10 ml) were stirred and heated under reflux for 4 h. The mixture was poured into ice–water, made basic with 5% aqueous sodium carbonate, and extracted with diethyl ether. The ether–benzene layer was separated, washed with water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure afforded an oil which was purified by flash column chromatography (50% hexanes–25% benzene–25% chloroform) to give the *methoxy compound* (**16a**) (0.326 g, 20%) as an oil (Found: M^+, 163.0735. $C_8H_9N_3O$ requires *M*, 163.0745); *m/z* 163, 119, 104, 91, 64, 45, and 28; $\nu_{max.}$ 1 449, 1 313, 1 201, 1 168, 1 152, 1 108, 1 083, 1 003, and 745 cm^{-1}; δ 3.42 (3 H, s), 6.10 (2 H, s), and 7.33—8.43 (4 H, m).

1-*Benzotriazol*-1-*yl*-1-*alkoxyalkanes* (**16b—i**): *General Procedure.*—Benzotriazole (2.38 g, 20 mmol), the aldehyde (30 mmol), the alcohol (60 mmol), sulphuric acid (1 drop), and carbon tetrachloride (30 ml) were refluxed for 3 h using a Soxhlet apparatus with $CaCl_2$ to trap water. In the case of acetaldehyde, the heating was carried out in a sealed tube. The mixture was poured into ice–water, made basic with sodium carbonate, and extracted with diethyl ether. The organic layer was separated, washed with water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure afforded an oil which was purified by flash column chromatography (50% hexanes–25% benzene–25% chloroform). Analytical and spectral data are collected in Table 2.

1-*Benzotriazol*-1-*yl*-2-*chloro*-1-*methoxyethane* (**17**).—Prepared from 2-chloro-1,1-dimethoxyethane (1.87 g, 15 mmol) and benzotriazole (1.19 g, 10 mmol) following the procedure described for (**16a**), purification by flash column chromatography (70% benzene–30% chloroform) gave the product (**17**) (0.635 g, 30%) as an oil (Found: C, 51.1; H, 4.8; N, 19.9. $C_9H_{10}ClN_3O$ requires C, 51.1; H, 4.8; N, 19.9%); $\nu_{max.}$ 2 958, 2 936, 2 831, 1 446, 1 332, 1 278, 1 152, 1 114, 1 091, 1 075, 1 030, 943, and 738 cm^{-1}; δ 3.41 (3 H, s), 4.21 (2 H, d, *J* 6.4 Hz), 6.27 (1 H, t, *J* 6.4 Hz), and 7.25—8.40 (4 H, m).

1,3-*Dibenzotriazol*-1-*yl*-1,3-*diethoxypropane* (**18**).—Benzotriazole (2.38 g, 20 mmol), malonaldehyde bis(diethylacetal) (2.39 ml; 10 mmol) and *p*-toluenesulphonic acid (0.02 g) were stirred and heated under nitrogen at 100 °C for 30 min. The reaction was monitored by ^1H n.m.r. spectroscopy. The crude material dissolved in chloroform was washed with 5% aqueous sodium carbonate, then with water and dried ($MgSO_4$). Evaporation afforded an oil which was subjected to flash column chromatography (80% chloroform–20% ethyl acetate) to give the title *compound* (**18**) as a 1:1 mixture of diastereoisomers (3.00 g, 82%), as an oil (Found: C, 62.0; H, 6.1; N, 22.8. $C_{19}H_{22}N_6O_2$ requires C, 62.3; H, 6.1; N, 22.9); $\nu_{max.}$ 1 441, 1 372, 1 331, 1 277, 1 154, 1 111, 1 089, 1 000, 933, and 746 cm^{-1}; δ 1.16 (6 H, t, *J* 6.9 Hz), 2.97—3.86 (6 H, m), 6.15 (1 H, t, *J* 6.8 Hz), 6.57 (1 H, t, *J* 5.9 Hz), and 7.23—8.37 (8 H, m).

3-*Benzotriazol*-1-*yl*-1,1-*dimethoxybutane* (**19**).—Benzotriazole (1.19 g, 10 mmol), crotonaldehyde (1.05 g, 15 mmol), methanol (1.2 ml, 30 mmol), sulphuric acid (1 drop), and benzene (15 ml) were stirred and heated under reflux for 3 h. The reaction mixture was poured into ice–water, neutralized with sodium hydrogen carbonate, and extracted with diethyl ether. The organic layer was washed with water, dried ($MgSO_4$), and the solvent evaporated under reduced pressure. Flash column chromatography of the resulting oil (40% benzene–40% chloroform–20% ethyl acetate) gave the title *compound* (**19**) (0.306 g, 13%) as an oil (Found: C, 61.6; H, 7.0. $C_{12}H_{17}N_3O_2$ requires C, 61.3; H, 7.3%); (Found: *m/z* 235.1306 (M^+). $C_{12}H_{17}N_3O_2$ requires *M*, 235.1321), 220, 204, 146, 134, 119, 118, 117, 104, 101, 92, 91, 85, 75, 59, 47, and 27; $\nu_{max.}$ 2 977, 2 932, 2 828, 1 451, 1 380, 1 272, 1 192, 1 164, 1 143, 1 121, 1 072, 1 050, 965, and 745 cm^{-1}; δ 1.74 (3 H, d, *J* 6.8 Hz), 2.43 (2 H, m), 3.26 (6 H, s), 4.10 (1 H, dd, *J* 4.7 and 6.9 Hz), 5.19 (1 H, sextet, *J* 6.8 Hz), and 7.17—8.33 (4 H, m).

3-*Benzotriazol*-1-*yl*-1,1-*diethoxybutane* (**20**).—This was prepared from benzotriazole (1.19 g, 10 mmol), crotonaldehyde (1.05 g, 15 mmol), and ethanol (1.76 ml; 30 mmol) following the procedure described for (**19**). Flash column chromatography of the crude oil (80% chloroform–20% ethyl acetate) gave the title *compound* (**20**) (1.40 g, 53%) as an oil (Found: C, 64.0; H, 7.7. $C_{14}H_{21}N_3O_2$ requires C, 63.9; H, 8.0%); *m/z* 263 (M^+), 234, 218, 144, 120, 118, 117, 103, 99, 91, 77, 75, 71, 47, and 29; $\nu_{max.}$ 2 923, 2 872, 1 439, 1 371, 1 267, 1 120, 1 054, and 738 cm^{-1}; δ 1.12 (6 H, t, *J* 6.9 Hz), 1.71 (3 H, d, *J* 6.9 Hz), 2.43 (2 H, m), 3.48 (4 H, m), 4.25 (1 H, m), 5.24 (1 H, m), and 7.27—8.33 (4 H, m).

4-*Benzotriazol*-1-*yl*-2,6-*diethyl*-5-*methyl*-1,3-*dioxane* (**21**).—Benzotriazole (5.95 g, 50 mmol), propionaldehyde (4.33 ml; 60 mmol), sulphuric acid (2 drops), and acetic acid (15 ml) were heated at 80 °C for 3 h. The mixture was poured into ice–water and extracted with diethyl ether. The organic layer was washed with water, 10% ammonia and twice more with water. The solution was dried over anhydrous $MgSO_4$ and the solvent was evaporated to give an oil (4.13 g) shown by t.l.c. to be a mixture of five compounds. Part of the oil was subjected to column chromatography ($CHCl_3$); first eluted was the title *compound* (**21**) (0.15 g, 9%) which crystallized from pentane ether (2:1) as needles, m.p. 97—98 °C (Found: C, 65.1; H, 8.0; N, 15.3. $C_{15}H_{21}N_3O_2$ requires C, 65.4; H, 7.7; N, 15.3%); $\nu_{max.}$ 2 975, 2 944, 2 882, 1 458, 1 449, 1 330, 1 275, 1 160, 1 148, 1 134, 1 126, 1 045, 960, and 748 cm^{-1}; δ 0.84 (3 H, t, *J* 7.2 Hz), 1.00 (3 H, t, *J* 7.0 Hz), 1.37 (3 H, d, *J* 7.4 Hz), 1.56 (4 H, q, *J* 7.2 Hz), 3.08 (1 H, dq, *J* 7.4 and 1.7 Hz), 4.40 (2 H, m), 6.14 (1 H, s), and 7.27—8.37 (4 H, m).

α-*Benzotriazol*-1-*ylbenzyl Acetate* (**24**).—Nitrogen was passed through benzotriazole (1.19 g, 10 mmol) and benzylidene diacetate[64] at 140 °C for 2.5 h. The reaction was monitored by n.m.r. spectroscopy and found to give the title *compound* (**24**) (1.87 g, 70%) as an oil (Found: M^+, 267.0992. $C_{15}H_{13}N_3O_2$ requires *M*, 267.1008); *m/z* 267, 208, 196, 180, 168, 161, 152, 133, 119, 107, 105, 91, 77, 64, 51, 43, and 28; $\nu_{max.}$ 1 758, 1 367, 1 237, 1 204, 1 057, 1 004, 951, and 744 cm^{-1}; δ 2.15 (3 H, s), and 7.33—8.70 (10 H, m).

2-*Acetoxy*-1-(*diacetoxymethyl*)*naphthalene* (**23**).—2-Hydroxynaphthalene-1-carbaldehyde (4.31 g, 25 mmol), acetic acid (10 ml), acetic anhydride (10 ml), and thionyl chloride (5 ml) were refluxed for 2 h and poured into ice–water. The mixture was extracted with chloroform and the extract washed with 5% aqueous sodium carbonate and then with water, dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The resulting oil was triturated with diethyl ether to give the title *compound* (**23**) (2.52 g, 32%) which crystallized from toluene as grains, m.p. 129—130 °C (Found: C, 64.9; H, 5.0. $C_{17}H_{16}O_6$ requires C, 64.6; H, 5.1%); $\nu_{max.}$ 1 759, 1 438, 1 367, 1 240, 1 198, 1 165, 1 087, 1 007, 978, and 966 cm^{-1}; δ 2.12 (6 H, s), 2.48 (3 H, s), 7.22—8.15 (5 H, m), and 8.68 (2 H, m).

Benzotriazol-1-*yl*(2-*acetoxy*-1-*naphthyl*)*methyl Acetate* (**25**).—Benzotriazole (0.67 g, 5.6 mmol) and (**23**) (0.98 g, 3.10 mmol) were heated under nitrogen at 125 °C for 3.5 h. Flash column chromatography (50% benzene–50% chloroform) followed by recrystallization from pentane-ether (1:1) afforded the *acetate* (**25**) (0.28 g, 24%) as microcrystals, m.p. 139—140 °C (Found: C, 67.1; H, 4.6; N, 10.9. $C_{21}H_{17}N_3O_4$ requires C, 67.2; H, 4.6; N, 11.2%); $\nu_{max.}$ 1 761, 1 368, 1 259, 1 206, 1 188, 1 079, 1 043, 1 010, 880, and 741 cm^{-1}; δ 2.33 (3 H, s), 2.47 (3 H, s), 7.47 (5 H, m), 7.95 (4 H, m), 8.53 (1 H, m), and 9.12 (1 H, m).

Benzotriazol-1-*ylmethyl Acetate* (**26**).—Benzotriazol-1-ylmethanol (7.46 g, 50 mmol) and acetic anhydride (10 ml) in acetic acid (20 ml) was kept at 60 °C for 24 h and then poured into ice–water. The mixture was made alkaline with 5% aqueous sodium hydroxide and extracted with chloroform. The chloroform layer was washed with water, dried ($MgSO_4$), filtered, evaporated under reduced pressure, and subjected to flash chromatography (50% benzene–50% chloroform). Crystallization of the main fraction from pentane afforded the title *compound* (**26**) (2.83 g, 30%) as granules, m.p. 58—59 °C (Found: C, 56.4; H, 4.7; N, 21.9. $C_9H_9N_3O_2$ requires C, 56.5; H, 4.7; N, 22.0%); $\nu_{max.}$ 1 755, 1 498, 1 454, 1 368, 1 213, 1 158, 1 030, 1 002, 973, 791, and 747 cm^{-1}; δ 2.13 (3 H, s), 6.68 (2 H, s), and 7.33—8.33 (4 H, m).

Benzotriazol-1-*ylmethyl Benzoate* (**27**).—To stirred benzotriazol-1-ylmethanol (3.75 g, 25 mmol) and 4-dimethylaminopyridine (DMAP) (0.306 g, 2.5 mmol) in pyridine (20 ml) kept at 5 °C was added dropwise benzoyl chloride (4.2 g, 30 mmol). The mixture was stirred at 5 °C for an additional 0.5 h and then kept at 0 °C for 12 h and poured into ice–water. The resultant precipitate was washed with water and recrystallized from methanol to give the title *compound* (**27**) (4.34 g, 68%) as needles, m.p. 91—92 °C (Found: C, 66.4; H, 4.3; N, 16.5. $C_{14}H_{11}N_3O_2$ requires C, 66.4; H, 4.4; N, 16.6%); $\nu_{max.}$ 1 725, 1 569, 1 488, 1 477, 1 255, 1 154, 1 080, 1 020, 982, 749, and 703 cm^{-1}; δ 6.9 (2 H, s), 7.23—7.83 (5 H, m), and 7.83—8.49 (4 H, m).

Note added in proof. We have since located a reference to the addition product of acetaldehyde and benzotriazole [V. Mozolis and S. J. Jokubaityte, *Liet. TSR Mokslu Akad. Darb., Ser. B*, 1970, **2**, 83 (*Chem. Abstr.*, 1971, **74** 35632)]

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