1-Bromo- and 1-Iodo-benzotriazoles

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1-Bromo- and 1-iodo-benzotriazoles are obtained from 1-chlorobenzotriazole and bromine and iodine respectively. The bromo-compound is a reactive oxidant and source of electrophilic bromine. Pentachlorobenzotriazole is more reactive than 1-chlorobenzotriazole in accord with its greater positive halogen character.

SEVERAL years ago we reported the extremely simple preparation of 1-chlorobenzotriazole (1) from benzotriazole and sodium hypochlorite in aqueous acetic acid.[1] The similar electronegativities of nitrogen and chlorine and the aromatic stabilisation of the benzotriazolyl anion combine to make 1-chlorobenzotriazole a positive halogen compound, and it has found use as a convenient oxidising agent [1,2] and as a source of electrophilic [3,4] (and radical) chlorine. It is a colourless, crystalline solid, soluble in most organic solvents (very soluble in dichloromethane, moderately soluble in benzene) and has a convenient shelf life.† In spite of the interest in and exploitation of 1-chlorobenzotriazole the corresponding bromo- (2) and iodo-compounds (3) have not been described. We now report their formation and some of their properties.

1-Bromobenzotriazole (2) is most conveniently prepared by the addition of 1-chlorobenzotriazole to a solution of bromine in dichloromethane. The bromo-compound crystallises from this mixture as a colourless solid, m.p. 113—114 °C (decomp.). Its i.r. spectral characteristics are very similar to those of 1-chlorobenzotriazole, the two peaks at 1 610 and 1 590 cm^{-1} are diagnostic for 1-substituted benzotriazoles and confirm that the bromine is on N-1. Attempted formation by the addition of sodium hypobromite to a solution of benzotriazole in aqueous acetic acid or addition of alkaline sodium hypobromite to benzotriazole in aqueous potassium carbonate gave an impure product which was difficult to purify. Pure 1-bromobenzotriazole has a similar stability to that of 1-chlorobenzotriazole.

1-Iodobenzotriazole (3) can also be obtained by treatment of 1-chlorobenzotriazole in dichloromethane with one equivalent of iodine. The initial product from this reaction is a pale yellow complex for which mass balance and elemental analysis indicates a stoicheiometry, iodobenzotriazole : iodine 3 : 1. Iodine can be removed from this complex by sublimation on heating to 150—160 °C, or better by dissolution in 2M-hydrochloric acid

† There have been reports of the instability of 1-chlorobenzotriazole, but in our experience the compound is quite stable for three months if properly purified and stored in dark bottles preferably in a refrigerator. Should discolouration occur its further storage is not recommended.

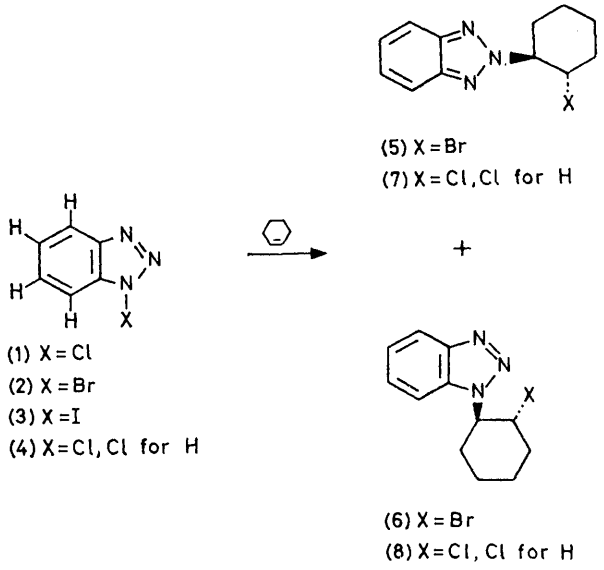
[1] C. W. Rees and R. C. Storr, *J. Chem. Soc.* (*C*), 1969, 1474.

[2] W. D. Kingsbury and C. R. Johnson, *Chem. Comm.*, 1969, 365; W. C. Ferrell and K.-C. Yao, *J. Lipid Res.*, 1972, **13**, 23; M. Cinquini and S. Colonna, *Synthesis*, 1972, 259; A. D. Dawson and D. Swern, *J. Org. Chem.*, 1977, **42**, 592.

[3] C. W. Rees and R. C. Storr, *J. Chem. Soc.* (*C*), 1969, 1478.

[4] K. V. Lichman, *J. Chem. Soc.* (*C*), 1971, 2539; A. Ledwith, P. M. Bowyer, and D. H. Iles, *J. Chem. Soc.* (*C*), 1971, 2775; H. Oelschlager and E. Ehlers, *Pharm. Acta Helv.*, 1972, **13**, 23.

followed by careful basification with potassium carbonate. The melting (decomposition) point of the iodo-compound, which is amorphous and extremely insoluble in organic



solvents, varies according to the method by which it is purified (254—256 or 214—216 °C). However the samples are otherwise identical and give satisfactory analytical data. I.r. absorptions at 1 610 and 1 590 cm^{-1} are again indicative of N-1 substitution. An alternative preparation of 1-iodobenzotriazole involving addition of a sodium hypoiodite solution to benzotriazole in aqueous sodium hydroxide and careful neutralisation with 2M-hydrochloric acid gave initially a dark blue precipitate. When set aside in contact with water this slowly decolourises to give 1-iodobenzotriazole identical in all respects with that obtained previously.

The solubility of the halogenobenzotriazoles in organic solvents decreases markedly from the chloro- to the bromo- and iodo-derivatives. This we attribute to the increased polarity of the nitrogen–halogen bond in the sense N(δ−)–X(δ+) which is to be expected as the electronegativity of the halogen decreases.[5] This leads to stronger dipolar interactions between the molecules which are less easily disrupted by a nonpolar solvent.

In accord with its increased polarity, 1-bromobenzotriazole is much more reactive than 1-chlorobenzotriazole in electrophilic addition to alkenes. The addition to cyclohexene is essentially instantaneous in dichloromethane at room temperature compared with a reaction time of *ca.* 4 h for the chloro-derivative despite the heterogeneous nature of the bromo-compound reactions because of its low solubility. The products of addition, *trans*-1-benzotriazol-2-yl-2-bromocyclohexane (5), m.p. 87—88 °C (41%), and the corresponding benzotriazol-1-yl isomer (6), m.p. 87 °C (29%), together with benzotriazole, closely parallel those from reaction of 1-chlorobenzotriazole with the same alkene. The *trans*-stereochemistry of addition for both adducts is apparent from their 220 MHz n.m.r. spectra which show triplets (J = 11 Hz) of doublets (J = 4.5 Hz) for each of the methine protons. Thus, in either adduct both methine protons are axial. The *trans*-stereoselectivity is consistent with polar addition *via* a bridged bromonium ion intermediate.

Initial experiments indicate that 1-bromobenzotriazole is an oxidant of similar scope to the 1-chloro-compound. However, with alcohols, although it is as or more reactive than 1-chlorobenzotriazole, it is somewhat less convenient to use since benzotriazole hydrobromide does not precipitate cleanly and it gives the carbonyl compound in lower yield (see Table).

Alcohol	Product	1-Chloro-benzotriazole	1-Bromo-benzotriazole
Cyclohexanol	Cyclohexanone	70% [a]	29% [b]
		52% (10 min) [b]	(10 min)
1-Phenyl-ethanol	Acetophenone	65% [a]	55% [b]
		58% (20 min) [b]	(10 min)
Benzyl alcohol	Benzaldehyde	80% [a]	50% [b]
		55% (8 h) [b]	(30 min)

[a] Optimum yield, ref. 1. [b] Yields obtained under comparable conditions using 0.25M solutions of alcohol and oxidant in dichloromethane.

The simple electronegativity arguments used to rationalise the reactivity and physical characteristics of the halogenobenzotriazoles point the way for the design of more reactive (or more selective) halogenoheterocycles. Thus one would anticipate that a chlorobenzotriazole derivative in which the benzotriazolyl anion would be specially stabilised by substituents should be more reactive than the unsubstituted 1-chlorobenzotriazole. This expectation is borne out. *N*,4,5,6,7-Pentachlorobenzotriazole (4) * is easily obtained by the action of sodium hypochlorite on an acetic acid solution of tetrachlorobenzotriazole. Again this compound, m.p. 169—171 °C (decomp.), is extremely insoluble in organic solvents but, nevertheless, is a reactive oxidant, and also undergoes rapid addition to alkenes; thus, cyclohexene gives the expected *trans*-chloro 1- and 2-substituted tetrachlorobenzotriazolyl adducts (7), m.p. 177—178 °C (34%), and (8), m.p. 196 °C (31%), respectively. Again the *trans*-stereochemistry of the adducts is apparent from the coupling of the methine protons in their ^1H n.m.r. spectra.

These ideas are being extended to monocyclic triazoles and other heterocyclic systems with the possibility of producing reagents superior to 1-chlorobenzotriazole.

EXPERIMENTAL

1-Bromobenzotriazole.—A solution of 1-chlorobenzotriazole (767 mg, 5 mmol) in dichloromethane (25 ml) was added to a solution of bromine (800 mg, 5 mmol) in dichloromethane

* We have been unable to assign unambiguously the fifth chlorine to N-1 or N-2 because of the lack of diagnostic i.r. absorptions in the tetrachlorobenzotriazole system and because of the extreme insolubility of compound (4) which precludes ^{13}C n.m.r. spectral studies. Differentiation on the basis of u.v. spectra was not possible because of the high reactivity of (4) towards the normal solvents.

[5] R. Hüttel and G. Welzel, *Annalen*, 1955, **593**, 207.

(50 ml). The orange solution was stirred for 5 min, and then carefully concentrated to *ca.* 10 ml under reduced pressure. This gave a precipitate of 1-*bromobenzotriazole* (810 mg, 80%), a colourless crystalline solid, m.p. 113—114 °C (decomp.) (Found: C, 36.3; H, 2.0; N, 21.5. $C_6H_4BrN_3$ requires C, 36.4; H, 2.0; N, 21.2%; *M* 197, 199), $\nu_{max.}$ 1 610, 1 589, 1 265, 1 213, 1 158, 1 001, 930, 788, 744, and 653 cm^{-1}; *m/e* 199, 197 (*M*, base peak), 171, and 169 ($M - N_2$).

Attempted preparation of 1-bromobenzotriazole by addition of bromine in aqueous sodium hydroxide to a solution of benzotriazole in aqueous potassium carbonate followed by neutralisation gave an impure orange solid that was difficult to purify. Similar results were obtained on addition of sodium hypobromite solution to benzotriazole in aqueous acetic acid.

1-*Iodobenzotriazole–Iodine Complex.*—A solution of 1-chlorobenzotriazole (767 mg, 5 mmol) in dichloromethane (10 ml) was added during 5 min to a rapidly stirred mixture of iodine (1.27 g, 5 mmol) and dichloromethane (50 ml). After 15 min the resulting precipitate was filtered off and washed with dichloromethane to give the complex (1.63 g, 99%) as a pale orange solid which decomposed at 140 °C with loss of iodine (Found: C, 22.6; H, 1.1; N, 12.8. $C_{18}H_{12}I_5N_9$ requires C, 21.9; H, 1.2; N, 12.8%), $\nu_{max.}$ 1 610, 1 588, 1 444, 1 268, 1 189, 1 166, 1 000, 927, 785, 749, and 648 cm^{-1}.

1-*Iodobenzotriazole.*—(*a*) The iodine complex (1.63 g, 5 mmol) was dissolved in 2M-hydrochloric acid (100 ml) whereupon iodine was liberated. Solid potassium carbonate was added until the solution was neutral, and the precipitate was filtered off and dried to give 1-*iodobenzotriazole* (1.13 g, 94%) as a buff solid, m.p. 214—216 °C (decomp.) (Found: C, 29.7; H, 1.6; N, 17.3. $C_6H_4IN_3$ requires C, 29.4; H, 1.6; N, 17.2%; *M* 245), $\nu_{max.}$ 1 610, 1 588, 1 444, 1 268, 1 189, 1 166, 1 000, 927, 785, 749, and 648 cm^{-1}; *m/e* 254 (I_2), 245 (*M*), and 217 ($M - N_2$).

(*b*) The finely ground iodine complex (1.8 g, 5.52 mmol) was heated at 150—160 °C in a Woods metal bath. Sublimation of iodine occurred, and after 30 min the residue of 1-iodobenzotriazole was collected (1.12 g, 84%), m.p. 254—256 °C (decomp.). The i.r. spectrum of this sample was identical with that obtained by method (*a*).

(*c*) A solution of iodine (762 mg, 3 mmol) in M-aqueous sodium hydroxide (10 ml) was added dropwise with stirring to a solution of benzotriazole (357 mg, 3 mmol) and potassium carbonate (415 mg, 3 mmol) in water (20 ml). A deep blue precipitate formed, which redissolved to give a yellow solution. This was neutralised by addition of 2M-hydrochloric acid and the resulting blue precipitate was quickly filtered off and added to water (100 ml). After the mixture had been stirred for several minutes the solid had decolourised and was allowed to settle. The supernatant liquid was decanted off and the solid was dried to give 1-iodobenzotriazole (350 mg, 43%), m.p. 216—219 °C.

A sample of the unstable blue solid after being dried in a desiccator had m.p. 90 °C (decomp.), $\nu_{max.}$ 1 313, 1 287, 1 269, 1 220, 1 153, 1 135, 1 121, 1 030, 1 002, 910, 791, and 745 cm^{-1}.

Reaction of 1-*Bromobenzotriazole with Cyclohexene.*—1-Bromobenzotriazole (594 mg, 3 mmol) was added to a stirred solution of cyclohexene (309 mg, 3.75 mmol) in dichloromethane (6 ml). An immediate exothermic reaction occurred, which was complete within 2 min. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel. Elution with 10% ether–petroleum gave trans-1-(*benzotriazol-2-yl*)-2-*bromocyclohexane* (345 mg, 41%) as colourless crystals, m.p. 87—88 °C from hexane (Found: C, 51.5; H, 5.1; N, 15.2. $C_{12}H_{14}BrN_3$ requires C, 51.4; H, 5.0; N, 15.0%; *M* 279, 281), $\nu_{max.}$ 1 569, 1 323, 1 280, 1 218, 1 190, 1 009, 979, 914, 890, 853, 742, 697, and 687 cm^{-1}; $\delta(CDCl_3)$ 7.99 (2 H, q, AA′XX′), 7.38 (2 H, q, AA′XX′), 4.96 (1 H, t of d, J = 11 and 4.5 Hz), 4.73 (1 H, t of d, J = 11 and 4.5 Hz), and 2.7—1.5 (8 H complex m); *m/e* 281, 279 (*M* base peak) and 200 (M − Br).

Elution with 30% ether–petroleum gave trans-1-(*benzotriazol-1-yl*)-2-*bromocyclohexane* (239 mg, 29%) as colourless crystals, m.p. 87 °C from ether–pentane (Found: C, 51.2; H, 4.9; N, 14.9. $C_{12}H_{14}BrN_3$ requires C, 51.5; H, 5.1; N, 15.2%; *M* 279, 281), $\nu_{max.}$ 1 612, 1 590, 1 233, 1 192, 1 173, 1 071, 982, 932, 822, 790, 777, 770, 751, and 697 cm^{-1}; $\delta(CDCl_3)$ 8.06 (1 H, d, J = 7.5 Hz), 7.60 (1 H, d, J = 7.5 Hz), 7.48 (1 H, t, J = 7.5 Hz), 7.36 (1 H, t, J = 7.5 Hz), 3.80—3.65 (2 H, two overlapping t of d, J = 11 and 4.5 Hz), and 2.7—1.5 (8 H, complex); *m/e* 281, 279 (*M* base peak), 253, 251 ($M - N_2$), and 200 (M − Br). Elution with ether gave benzotriazole (69 mg, 20%).

Oxidation of Alcohols with 1-*Bromobenzotriazole.*—1-Bromobenzotriazole (495 mg, 2.5 mmol) was added to a solution of the alcohol (3 mmol) in dichloromethane (10 ml), and the mixture was warmed on a steam-bath. An orange-yellow colouration developed in the solution, which turned pale yellow at the end of the reaction. The bromo-compound gradually dissolved during the course of the reaction.

The cooled solution was extracted with aqueous sodium carbonate to remove benzotriazole hydrobromide, and the aldehyde solution was estimated by preparation of the 2,4-dinitrophenylhydrazone. To the solution was added five drops of concentrated hydrochloric acid, and a solution of 2,4-dinitrophenylhydrazine (750 mg) in ethanol (50 ml). After the solution had been boiled for 2 min, the precipitate of the hydrazone was collected and recrystallised from ethanol.

Cyclohexanol (10 min reaction time) gave cyclohexanone 2,4-dinitrophenylhydrazone (205 mg, 29%), m.p. 156—158 °C (lit., m.p. 160 °C), from ethanol. Benzyl alcohol (30 min reaction time) gave benzaldehyde 2,4-dinitrohydrazone (360 mg, 50%), m.p. 235—236 °C (lit., 237 °C) from ethanol. 1-Phenylethanol (10 min reaction time) gave acetophenone 2,4-dinitrophenylhydrazone (435 mg, 55%), m.p. 240—241 °C (lit., 240 °C), from ethanol.

The above reactions were repeated under the same conditions using 1-chlorobenzotriazole which was completely soluble. Benzotriazole hydrochloride was filtered off but work-up was otherwise identical. Yields and reaction times are given in the Table.

Pentachlorobenzotriazole.—Sodium hypochlorite (0.9M; 9 ml) was added dropwise with stirring to a solution of 4,5,6,7-tetrachlorobenzotriazole (2.0 g, 7.7 mmol) in glacial acetic acid (50 ml). After 3 min, the precipitate was filtered off, washed thoroughly with water, and dried in a desiccator to give *N*,4,5,6,7-*pentachlorobenzotriazole* (1.5 g, 66%) as a colourless solid, m.p. 169—171 °C (decomp.), $\nu_{max.}$ 1 298, 1 243, 1 229, 1 191, 1 042, 1 025, 984, 835, and 814 cm^{-1}; *m/e* 299, 297, 295, 293, 291, and 289 (*M* base peak), $C_6Cl_5N_3$ requires *m/e* ^{35}Cl 289. A satisfactory microanalysis was not obtained. Attempted recrystallisation from ethyl

acetate–petroleum gave 4,5,6,7-tetrachlorobenzotriazole, m.p. and mixed m.p. 256—258 °C (lit.,[6] 256—260 °C).

Reaction of Pentachlorobenzotriazole with Cyclohexene.—Pentachlorobenzotriazole (1.164 g, 4 mmol) was added to a stirred solution of cyclohexene (412 mg, 5 mmol) in dichloromethane (8 ml). An immediate exothermic reaction occurred, which was complete within 2 min. The precipitate of 4,5,6,7-tetrachlorobenzotriazole (156 mg) was filtered off and crystallised from methanol to give prisms, m.p. 261 °C. The remaining solution was evaporated and the residue was chromatographed on silica gel. Elution with 10% ether–petroleum gave trans-1-*chloro*-2-(4,5,6,7-*tetrachlorobenzotriazol*-2-*yl*)*cyclohexane* (467 mg, 31%) as colourless needles, m.p. 196 °C from hexane (Found: C, 38.6; H, 2.7; N, 11.0. $C_{12}H_{10}Cl_5N_3$ requires C, 38.6; H, 2.7; N, 11.2%; *M* ^{35}Cl 371), $\nu_{max.}$ 1 302, 1 280, 1 219, 1 116, 1 032, 1 015, 984, 923, 852, 842, 833, 810, 746, and 675 cm^{-1}; $\lambda_{max.}$ (ethanol) 222 (log ε 4.55), 294 (4.10), and 303 (4.09) nm; δ($CDCl_3$) 4.91 (1 H, t of d, J = 11 and 4.5 Hz), 4.61 (1 H, t of d, J = 11 and 4.5 Hz), and 3.6—2.3 (8 H, complex m); *m/e* 381, 379, 377, 375, 373, 371 (*M*, base peak), 344, 342, 340, 338, and 336 (*M* − Cl).

Continued elution with 10% ether–petroleum gave trans-1-*chloro*-(4,5,6,7-*tetrachlorobenzotriazol*-1-*yl*)*cyclohexane* (512 mg, 34%) as colourless crystals, m.p. 177—178 °C, from hexane (Found: C, 38.8; H, 2.7; N, 11.2. $C_{12}H_{10}Cl_5N_3$ requires C, 38.6; H, 2.7; N, 11.2%), $\nu_{max.}$ 1 590, 1 230, 1 158, 1 135, 1 072, 993, 971, 910, 853, 842, 790, 747, and 673 cm^{-1}; $\lambda_{max.}$ (ethanol) 221 (log ε 4.54), 275 (3.90), 283 (3.92), and 306 nm (3.71); δ($CDCl_3$) 5.41 (1 H, t of d, J = 11 and 4.5 Hz), 5.60 (1 H, t of d, J = 11 and 4.5 Hz), and 3.6—1.5 (8 H complex); *m/e* 381, 379, 377, 375, 373, 371 (*M*, base peak), 344, 342, 340, 338, 336 (*M* − Cl), 316, 314, 312, 310, and 308 (*M* − Cl − N_2). Elution with 50% ether–petroleum gave further 4,5,6,7-tetrachlorobenzotriazole (144 mg) (total yield 35%).

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[6] R. H. Wiley, K. H. Hussing, and J. Moffat, *J. Amer. Chem. Soc.*, 1955, **77**, 5105.