Conversions by Dimethyldioxirane of 1-Alkylbenzotriazoles into Their *N*-Oxides and of 2-Alkylbenzotriazoles into 2-Alkyl-*trans*-4,5,6,7-diepoxy-4,5,6,7-tetrahydrobenzotriazoles

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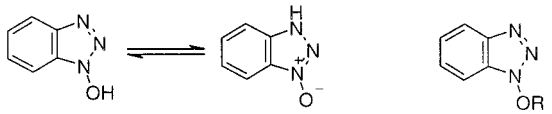
Dimethyldioxirane converted 1-alkylbenzotriazoles **4** to the corresponding 3-alkylbenzotriazole 1-oxides **5** in good yields, but transformed 2-alkylbenzotriazoles **12** into 2-alkyl-*trans*-4,5,6,7-diepoxy-4,5,6,7-tetrahydrobenzotriazoles **13**.

Introduction

A benzotriazole group in a molecule is known to behave as (i) an activator for proton loss,[1] (ii) a cation stabilizer, (iii) a leaving group, and (iv) a radical precursor.[2] These properties of a benzotriazole moiety were utilized in numerous studies aimed at developing efficient syntheses of organic compounds.[3] Although *O*-acyl derivatives of 1-hydroxybenzotriazole are of considerable synthetic use,[4−6] there has been little investigation of the *N*-oxides of *N*-alkylbenzotriazoles. The present work was planned to develop a reliable synthetic pathway to *N*-alkylbenzotriazole *N*-oxides and to study the ability of an oxidized benzotriazolyl group to serve as a nucleofuge.

Previously, three synthetic approaches to 3-substituted benzotriazole 1-oxides **5** have been reported. (a) The N-alkylation of 1-hydroxybenzotriazole (**1**) (which gave mixtures of **5** with 1-alkoxybenzotriazoles **3**) was chronologically the first,[7a,b] and has been further investigated.[8] (b) Closely related are the isomerizations of 1-alkoxybenzotriazoles (**3**) into **5** in refluxing chloroform[9] and the rearrangements of 1-benzoyloxybenzotriazoles[10] and 1-(α,*β*-unsaturated acyloxy)benzotriazoles.[11] (c) The reaction of 2-chloronitrobenzene with methylhydrazine gave 3-methylbenzotriazole 1-oxide **5a** along with various other products.[12]

Scheme 1



1 **2** **3**

1-Hydroxybenzotriazole (**1**) and 3*H*-benzotriazole 1-oxide (**2**) (Scheme 1) exist in a tautomeric equilibrium, which has been much studied by physical methods.[13,14] The position of the equilibrium depends on the solvent; e.g., in water the *N*-oxide form dominates.[15a,b] The NMR[15b] and mass spectra[15a] of benzotriazole 1-oxides have been reported.

To the best of our knowledge, no direct N-oxidations of 1-alkylbenzotriazoles have been previously recorded, although 1-substituted 1,2,3-triazoles were oxidized to the corresponding *N*-oxides using *m*-chloroperbenzoic acid.[16] 2-Methylbenzotriazole 1-oxide was obtained by oxidation of 2-methylbenzotriazole, however, in only 0.2% yield.[14] In the present work, we studied the direct oxidation of 1- and 2-alkylbenzotriazoles by dimethyldioxirane (DMD), known to be an effective oxidizing agent for N-oxidation of pyridines,[17,18] imines,[19] and tertiary amines.[18]

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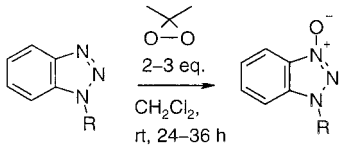
Scheme 2[a]



4a-l **5a-l**

[a] See Table 1 for R.

Table 1. Synthesis of *N*-Oxides 5 via Oxidation of Alkylbenzotriazoles by DMD (Method B)

compd	R	DMD (equiv)	reaction time, h	yield, %
5a	Me	2.0	24	90
5b	Et	2.0	24	74
5c	*n*-Pr	2.0	24	76
5d	*n*-C_6H_{13}	2.0	34	81
5e	*n*-C_9H_{19}	3.0	48	90
5f	CH_2Ph	3.0	48	92
5g	CH_2CH_2Ph	2.2	48	92
5h	CHPhMe	2.0	48	73
5i	CH_2CO_2Et	3.0	36	68
5j	CH_2OPh	3.0	36	91
5k	$CH_2C{\equiv}CH$	3.0	60	35
5l	CH_2CN	3.0	60	40
5m	COPh	2.0	48	0

Results and Discussion

Our study demonstrated that 1-alkyl- and 2-alkylbenzotriazoles on treatment with DMD show completely divergent chemical behavior. Reactions of 1-alkylbenzotriazoles **4a**−**l** with DMD led to N-oxidation to give the corresponding 3-alkylbenzotriazole 1-oxides **5a**−**l** (Scheme 2, Table 1). By contrast, 2-alkylbenzotriazoles **12a**,**b** underwent oxidation of the aromatic ring to give previously unknown *trans*-4,5,6,7-diepoxy-4,5,6,7-tetrahydrobenzotriazoles **13a**,**b** (Scheme 7).

Oxidation of 1-Alkylbenzotriazoles. We oxidized a number of 1-alkylbenzotriazole derivatives **4** with DMD using two alternative methods. In method A, 1-methylbenzotriazole **4a** was treated with a 0.08 M solution of DMD in acetone.[20] This led to the corresponding 3-methyl 1-oxide **5a** in 42% yield after purification by column chromatography on silica gel. The DMD solution was added to the substrate in two or three portions at 18 h intervals. The consumption of **4a** was monitored by TLC. Even with a 3-fold molar excess of the oxidizer, a significant amount of unreacted **4a** remained in the crude reaction mixture containing **5a**. In method B, 1 equiv of a 0.2−0.3 M solution of DMD in CH_2Cl_2[21] was used; after 12−18 h, the solvent was evaporated and another equivalent of DMD was added. In the cases of conversions of **4e** to **5e** and **4f** to **5f**, the evaporation and the addition of DMD were repeated to complete the reaction. Method B, while providing good to excellent yields of products, required an additional step for the preparation of the concentrated DMD solution. The yields obtained by method B are summarized in Table 1. The reaction tolerates various alkyl, functionalized alkyl, and arylalkyl substituents. However, electron-withdrawing groups in the starting benzotriazoles **4i**, **4k**, and **4l** reduce the yields (Table 1). Electron-deficient 1-benzoylbenzotriazole **4m** was inert to DMD.

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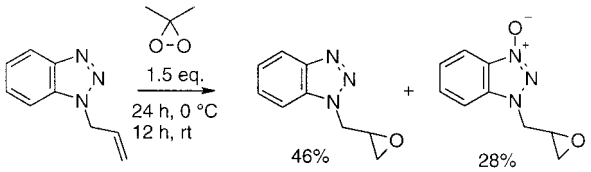
Scheme 3



4n **6** **7**

The oxidation of 1-substituted benzotriazoles by DMD is complicated by the presence of a C=C double bond in the structure. Whereas DMD rapidly oxidizes pyridines and tertiary amines selectively at 0 °C into their *N*-oxides in the presence of C=C bonds,[18] in contrast, 1-allylbenzotriazole (**4n**) is preferentially oxidized at the C=C bond slowly at 0 °C for 24 h. Complete conversion of 1-allylbenzotriazole occurred only at 20 °C and gave a mixture of 1-(2-oxiranylmethyl)-1*H*-benzotriazole **6** (46%) and 3-(2-oxiranylmethyl)-3*H*-benzotriazole 1-oxide **7** (28%) (Scheme 3). Evidently, the epoxide **6** formed first underwent further oxidation to **7**. As expected, 1-alkylbenzotriazoles are less reactive toward DMD compared to pyridines and tertiary amines,[18] which are easily oxidized at 0 °C.

Structure of 3-Substituted Benzotriazole 1-Oxides. The ^{13}C NMR spectrum ($CDCl_3$) obtained for 3-methylbenzotriazole 1-oxide **5a** matches that described previously.[15b] The signal of C-7a, although eclipsed by that of C-5, was revealed by APT. The ^1H NMR spectrum ($CDCl_3$) of 3-methylbenzotriazole 1-oxide **5a** differs significantly from that of **4a**: thus, the methyl group resonance (4.10 ppm) of 3-methylbenzotriazole 1-oxide **5a** was 0.20 ppm upfield compared to that of 1-methylbenzotriazole **4a**. The aromatic protons of **5a** are well resolved due to the shielding effect of N−O group, four separate groups of peaks appearing at: 7.36−7.44 (m, 1H, H-5), 7.49 (d, J = 8.5 Hz, 1H, H-4), 7.58−7.66 (m, 1H, H-6), 8.00 (d, J = 8.5 Hz, 1H, H-7). This characteristic pattern is repeated in the proton spectra of each of the 3-substituted benzotriazole 1-oxides **5**, except for those containing an aromatic ring in the 3-substituent (**5f**−**h**,**j**). For **5f**−**h**,**j**, the doublet for H-7 and the multiplet for H-6 are clearly separated, while the signals for H-4 and H-5 are covered under the multiplets of the 3-substituent phenyl ring.

The structure of 3-methylbenzotriazole 1-oxide **5a**, crystallized as a hemihydrate, was determined by single-crystal X-ray crystallography (Figure 1). The water molecule lies on a 2-fold crystallographic rotation axis and connects two molecules of the *N*-oxide by linear intermolecular hydrogen bonds. The molecular geometry of the *N*-oxide molecule is very similar to that of the parent 3*H*-benzotriazole 1-oxide **2**.[22] In each case, the N3−N2 bond is significantly longer than the N2−N1 bond.

The Reactivity of 3-Substituted Benzotriazole 1-Oxides. A strong nucleophile, thiophenol anion, did not displace the benzotriazole 1-oxide residue in **5f** on refluxing in ethanol or toluene for up to 36 h; in both cases, the starting material **5f** was recovered. Conversion of

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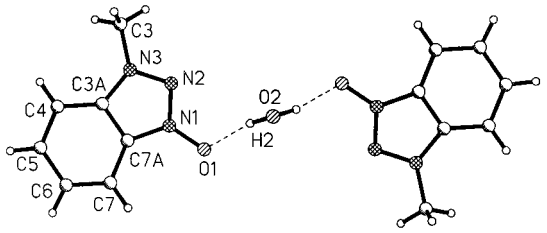
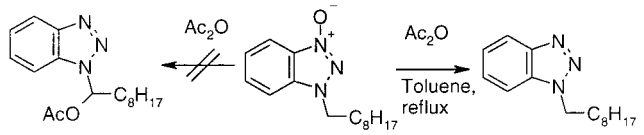


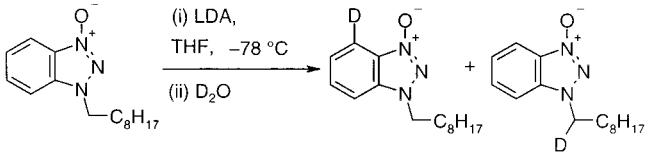
Figure 1. X-ray structure of **5a,** showing the intermolecular hydrogen bonding. The asymmetric unit is labeled. Selected interatomic distances (Å) and angles (deg): O1−N1, 1.295(1); N1−N2, 1.316(2); N2−N3, 1.345(2); N3−C3, 1.448(2); H2−O2, 0.88(2); H2−O1, 1.98(2); O1···O2, 2.848(1); O1−N1−N2, 121.5-(1); N1−N2−N3, 105.7(1); N2−N3−C3, 119.5(1); O2−H1···O2, 169(1).

Scheme 4



8 **5e** **4e**

Scheme 5



5e **9** **10**

the benzotriazole **4f** into the corresponding *N*-oxide **5f** thus does not increase its nucleofugacity sufficiently to allow easy displacement from an unactivated benzyl group.

Refluxing **5e** in neat acetic anhydride gave deoxygenated 1-nonylbenzotriazole **4e**. No appreciable loss of the nonyl group as nonylaldehyde or conversion of **5e** into 1-benzotriazolyl nonyl acetate **8** occurred (Scheme 4). For comparison, reaction of 2-methylpyridine *N*-oxide with acetic anhydride leads to the corresponding 2-pyridinylmethyl acetate.[23]

In a study of the lithiation of benzotriazole 1-oxides **5** with a strong base, 3-nonylbenzotriazole 1-oxide (**5e**) was treated with LDA in THF at −78 °C for 15 min and then quenched with D_2O. The ^1H NMR spectrum of the product showed that deuterium was incorporated roughly in ca. 90% at the 7-position of the benzotriazole 1-oxide ring and only partially (ca. 5%) in the α position of the benzotriazole 1-oxide alkyl chain to give **9** and **10**, respectively (Scheme 5). Incorporation of deuterium in the 4-position was not observed. This shows that the 1-position N−O group greatly increases the rate of lithiation of the 7-position CH, possibly by coordination in the transition state. 1-*n*-Alkylbenzotriazoles are lithiated mainly at the CH_2 group adjacent to N as shown by subsequent reactions of the anions formed with electrophiles.[1] However, 1-isopropylbenzotriazole undergoes lithiation predominantly at the benzenoid ring in the

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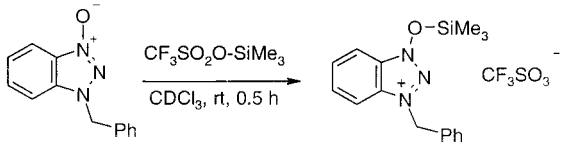
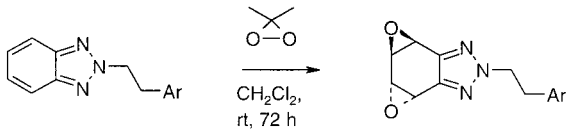
Scheme 6



5f **11**

Scheme 7



12a,b **13a** (50%); **13b** (77%)

a: Ar = Ph; **b**: Ar = *p*-$O_2NC_6H_4$

4-position (ca. 32%), 7-position (ca. 8%), and less (ca. 2%) at $CH(CH_3)_2$ adjacent to N.[24]

N-Oxide **5f** reacted with trimethylsilyl trifluoromethanesulfonate in $CDCl_3$ solution to give in situ 1-(trimethylsilyloxy)-3-benzylbenzotriazolium trifluoromethanesulfonate (**11**) (Scheme 6). Compound **11** was characterized by NMR: the ^1H spectrum shows the resonance of the CH_2 adjacent to N shifted downfield to 5.95 ppm compared to 5.57 ppm for *N*-oxide **5f**. The changes in ^{13}C NMR chemical shifts are even more pronounced. For example, CH_2 signals are shifted downfield to 55.7 ppm compared to 52.7 ppm for the parent *N*-oxide; C-7 and C-4 showed similar chemical shifts at 113.3 and 113.2 ppm; resonances of C-6 and C-5 appeared at 131.0 and 130.0 ppm, the chemical shifts of C-7a and C-4a were 130.8 and 130.4 ppm. This indicated that the positive charge in the benzotriazolium ring is now evenly distributed between N-1 and N-3 atoms.

Oxidation of 2-Alkylbenzotriazoles. In contrast to the conversion of 1-alkylbenzotriazoles (**4a**−**l**) into 3-alkylbenzotriazole 1-oxides (**5a**−**l**), a 2-fold excess of DMD in methylene chloride at ambient temperature converted 2-alkylbenzotriazoles **12a**,**b** into the corresponding *trans*-4,5,6,7-diepoxy-4,5,6,7-tetrahydrobenzotriazoles **13a**,**b** (Scheme 7). The NMR spectra of the reaction mixtures showed only the diepoxides **13a**,**b** along with unreacted **12a**,**b**, but no products of N-oxidation or other side reactions. Compounds **13a**,**b** were isolated using column chromatography on silica gel. They are quite stable and can be stored neat in air or in $CDCl_3$ solution at ambient temperature without any sign of decomposition for weeks. In contrast, *trans*-5,6,7,8-diepoxy-5,6,7,8-tetrahydroquinoline is reported to be unstable in the air.[25]

The trans orientation of the epoxide rings in **13** was assigned unambiguously from the vicinal coupling constants of the position 5 and 6 protons. Coupling constants obtained by analysis of the AA′BB′ system observed for the compounds **13** are comparable to those published for *trans*-1,2,3,4-diepoxy-1,2,3,4-tetrahydronaphthalene (**14**)[26]

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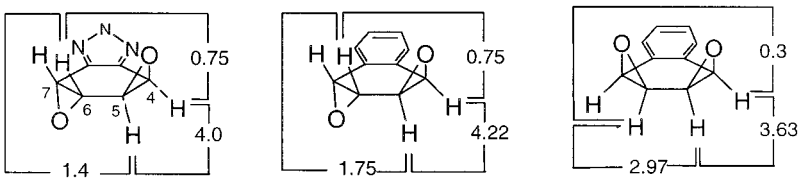

13a **14** **15**

Figure 2. Coupling constants obtained from simulation of spectra for compound **13a** and those for two isomers of naphthalene dioxide **14** and **15**.[26]

(Figure 2). Although both vicinal coupling constants $J_{4,5}$ and $J_{5,6}$ in **13** are slightly smaller than those in **14**, a coupling constant of $J_{5,6} = 1.4$ Hz is much closer to the corresponding coupling constant for trans protons in **14** (1.75 Hz) than to that for cis protons in *cis*-naphthalene dioxide **15** (2.97 Hz) (Figure 2).[26]

Arene oxides are of considerable interest due to their relationship to certain polycyclic aromatic hydrocarbons (PAH) possessing mutagenic and carcinogenic properties.[27] Naphthalene is converted by DMD into *trans*-1,2,3,4-diepoxy-1,2,3,4-tetrahydronaphthalene (**14**) in only 5% yield;[28] however, the more reactive methyl(trifluoromethyl)dioxirane gave a 90% conversion.[29] Compounds of type **13**, diepoxybenzenes fused with a triazole ring, which have not previously been reported, are of potential interest for their mutagenic/carcinogenic activity.[27,30]

Conclusion

We studied the oxidation of alkylbenzotriazoles by dimethyldioxirane in dichloromethane solution. Oxidation of 1-alkylbenzotriazoles **4** by DMD is a highly efficient synthetic pathway to the corresponding 3-alkylbenzotriazole 1-oxides **5**. The reaction is not applicable to compounds containing oxidizable substituents. Position 7 in 3-alkylbenzotriazole 1-oxides **5** is activated toward proton loss under the action of a strong base. The oxygen atom in 3-alkylbenzotriazole 1-oxides can be silylated to form trimethylsilyloxybenzotriazolium salt or removed by reflux with acetic anhydride. Oxidation of 2-alkylbenzotriazoles **12** by DMD led to the 2-alkyl-*trans*-4,5,6,7-diepoxy-4,5,6,7-tetrahydrobenzotriazoles **13**, described here for the first time.

Experimental Section

General Comments. Melting points were determined on a MEL-TEMP capillary melting point apparatus equipped with a Fluke 51 digital thermometer, and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in $CDCl_3$ referenced to Me_4Si for the ^{1}H spectra and $CDCl_3$ for the ^{13}C spectra. Tetrahydrofuran was distilled under nitrogen from sodium−benzophenone immediately before use. All reactions with moisture-sensitive compounds were carried out in dry nitrogen atmosphere. The 1- and 2-alkyl-1*H*-1,2,3-benzotriazoles were prepared according to the previously reported procedures.[31] Dimethyldioxirane solutions were prepared as described previously;[20,21] a detailed experimental procedure is included in the Supporting Information.

General Procedure for the Oxidation of Alkylbenzotriazoles (Method B). Alkylbenzotriazole (1 mmol, 5 mL) was placed in a dry flask, dissolved in 0.2 M solution of DMD (1 mmol) in dichloromethane, and stirred at room temperature for 18 h. The solvent was removed, and another equivalent of the DMD solution was added. The reaction was monitored by TLC. If necessary, a third equivalent of DMD was added (see Table 1). After another 12−18 h, the solvent was removed to give a brown oil, which was purified either by column chromatography using 25−30% acetone in pentane or by recrystallization from ethyl acetate.

3-Methyl-3*H*-1,2,3-benzotriazole 1-oxide (5a): brown prisms (90%) (from ethyl acetate); mp 142−145 °C; ^{1}H NMR δ 4.10 (s, 3H), 7.36−7.44 (m, 1H), 7.49 (d, J = 8.5 Hz, 1H), 7.58−7.66 (m, 1H), 8.00 (d, J = 8.5 Hz, 1H); ^{13}C NMR δ 34.6, 110.1, 115.7, 124.2, 130 (2C), 134.4. Anal. Calcd for $(C_7H_7N_3O)_2 \cdot H_2O$: C, 53.16; H, 5.10; N, 26.57. Found: C, 53.44; H, 5.16; N, 26.66.

Crystal data for 5a: $C_7H_7N_3O \cdot 0.5H_2O$, FW 158.16, monoclinic, space group $C2/c$, a = 20.451(7) Å, b = 6.767(2) Å, c = 13.471(4) Å, β = 129.259(3)°, V = 1443(1) Å^3, $F(000)$ = 664, Z = 8, T = −110 °C, μ(Mo Kα) = 0.11 mm^{-1}, D_{calcd} = 1.456 g·cm^{-3}, $2\theta_{max}$ 53° (CCD area detector, Mo Kα radiation), GOF = 1.07, wR(F^2) = 0.105 (all 1472 data), R = 0.034 (1212 data with $I > 2\sigma I$).

Oxidation of 1-Allyl-1*H*-benzotriazole (4n). 1-Allylbenzotriazole (0.40 g, 2.5 mmol) was placed in a dry flask, dissolved in 0.3 M solution of DMD (2.5 mmol, 8.3 mL) in CH_2Cl_2, and kept at 0 °C for 24 h. The reaction was monitored by TLC. The mixture was warmed to room temperature and kept for 6 h. Another portion of DMD (4.1 mL, 1.2 mmol) was added. After the disappearance of the starting material, the solvent was removed to give a mixture of **6** and **7** as brown oil, the components were separated by column chromatography on silica gel using 25−30% acetone in pentane as an eluent.

1-(2-Oxiranylmethyl)-1*H*-1,2,3-benzotriazole (6): yellow oil (46%); ^{1}H NMR δ 2.63 (bs, 1H), 2.90 (t, J = 3.6 Hz, 1H), 3.38−3.46 (m, 1H), 4.57 (dd, J = 15.0, 6.0 Hz, 1H), 5.09 (dd, J = 15.0, 1.9 Hz, 1H), 7.32−7.42 (m, 1H), 7.44−7.54 (m, 1H), 7.67 (d, J = 8.2 Hz, 1H), 8.04 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 45.0, 50.1, 50.2, 109.9, 119.6, 124.0, 127.5, 133.4, 145.8. Anal. Calcd for $C_9H_9N_3O$: N, 23.99. Found: N, 23.75.

3-(2-Oxiranylmethyl)-3*H*-1,2,3-benzotriazole 1-oxide (7): yellow prisms (from acetone/pentane) (29%); mp 85−87 °C; ^{1}H NMR δ 2.71 (t, J = 2.3 Hz, 1H), 2.90−2.98 (m, 1H), 3.37−3.46 (m, 1H), 4.37 (dd, J = 15.1, 6.2 Hz, 1H), 4.82 (dd, J = 15.1, 2.4 Hz, 1H), 7.35−7.45 (m, 1H), 7.56−7.70 (m, 2H), 7.95 (d, J = 8.4 Hz, 1H); ^{13}C NMR δ 45.2, 49.8, 50.7, 111.1, 115.3, 124.4, 130.3, 130.5, 134.5. Anal. Calcd for $C_9H_9N_3O_2$: C, 56.54; H, 4.74; N, 21.98. Found: C, 56.33; H, 4.97; N, 21.82.

Deoxygenation of 3-nonyl-3*H*-1,2,3-benzotriazole 1-Oxide (5e). 3-Nonyl-3*H*-1,2,3-benzotriazole 1-oxide (0.10 g, 0.38 mmol) was dissolved in Ac_2O (5 mL) and heated under reflux for 48 h. The excess acetic anhydride was destroyed by treatment with water. The cooled mixture was extracted with CH_2Cl_2, washed with aqueous Na_2CO_3 (saturated solution). The organic layer was dried over $MgSO_4$. Evaporation of the solvent produced a yellow oil that appears to have NMR spectra and R_f on TLC identical with those for compound **4e**.

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Deprotonation of 3-Nonyl-3*H*-1,2,3-benzotriazole 1-Oxide (5e). 3-Nonyl-3*H*-1,2,3-benzotriazole 1-oxide (0.10 g, 0.38 mmol) was dissolved in dry THF (10 mL) and cooled to −78 °C, and a 2 M solution of LDA (0.23 mL, 0.46 mmol) was added dropwise. The mixture was kept for 15 min at this temperature before D_2O (2 mL) was added. The mixture was allowed to warm to room temperature, and the organic phase was separated, dried over $MgSO_4$, and evaporated to give a brown oil as a mixture of compounds **9** (90%) and **10**. The NMR spectrum was recorded for the oil obtained.

7-Deuterio-3-nonyl-1*H*-1,2,3-benzotriazole 1-oxide (9): ^{1}H NMR δ 0.87 (t, J = 6.6 Hz, 3H), 1.16−1.40 (m, 12H), 1.90−2.08 (m, 2H), 4.38 (t, J = 7.1 Hz, 2H), 7.38 (d, J 6.9 Hz, 1H), 7.47 (d, J = 8.7 Hz, 1H), 7.54−7.66 (m, 1H); ^{13}C NMR δ 14.0, 22.6, 26.5, 28.9, 29.1, 29.2, 29.3, 31.8, 48.6, 110.1, 115.6 (t, J = 26.3), 124.0, 130.1 (2C), 133.9.

3-(1-Deuteriononyl)-1*H*-1,2,3-benzotriazole 1-oxide (10): ^{1}H NMR δ 0.87 (t, J = 6.6 Hz, 3H), 1.16−1.40 (m, 12H), 1.90−2.08 (m, 2H), 4.38 (t, J = 7.1 Hz, 1H), 7.30−7.40 (m, 1H), 7.41−7.48 (m, 1H), 7.57−7.70 (m, 1H), 8.00 (d, J = 8.7 Hz, 1H).

Synthesis of 1-(Trimethylsilyloxy)-3-benzyl-3*H*-1,2,3-benzotriazolium Trifluoromethanesulfonate (11). 3-Benzyl-3*H*-1,2,3-benzotriazole 1-oxide (**5f**) (0.05 g, 0.22 mmol) was dissolved in $CDCl_3$ (0.7 mL) in an NMR tube, trimethylsilyl trifluoromethanesulfonate (0.04 mL, 0.24 mmol) was added at room temperature; the tube was shaken well and kept for 30 min before NMR spectra were recorded. An attempt to isolate the neat compound **11** by evaporation of $CDCl_3$ led to a brown oil: ^{1}H NMR δ 5.95 (s, 2H), 7.34−7.50 (m, 5H), 7.72−7.88 (m, 3H), 7.98−8.04 (m, 1H); ^{13}C NMR δ 55.7, 113.2, 113.3, 128.6, 129.5, 129.9, 130.4, 130.8, 131.1, 132.3, 133.9. (Note: signals for TMS group are obscured by excess starting reagent).

2-(2-Phenylethyl)-*trans*-4,5,6,7-diepoxy-4,5,6,7-tetrahydrobenzotriazole (13a). This compound was prepared according to the general procedure (method B) except that 2 equiv of DMD was used. After 48 h, the solvent was removed and another 2 equiv of DMD solution was added. After 24 h, the solvent was removed, and the product was purified by column chromatography using ether and pentane as an eluent to give a yellow oil (50%): ^{1}H NMR δ 3.24 (t, J = 7.8 Hz, 2H), 3.89 (^{4}H, ^{7}H) and 3.98 (^{5}H, ^{6}H) (AA′BB′, $J_{4,5}$ = 4.0, $J_{4,6}$ = 0.75, $J_{4,7}$ = 0 Hz, $J_{5,6}$ = 1.4, $J_{5,7}$ = 0.75, $J_{6,7}$ = 4.0 Hz, 4H), 4.59 (t, J = 7.8 Hz, 2H), 7.12−7.20 (m, 2H), 7.20−7.34 (m, 3H); ^{13}C NMR δ 36.1, 45.4 (2C), 53.9 (2C), 56.4, 126.9, 128.6 (2C), 128.7 (2C), 137.0, 140.8 (2C). Anal. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46. Found: C, 65.76; H, 5.23; N, 16.57.

Supporting Information Available: Detailed procedure for the preparation of concentrated DMD solution in CH_2Cl_2, characterization data for the compounds **5b**−**l** and **13b**, details of the X-ray crystal structure of **5a**, and ^{1}H and ^{13}C NMR spectra of all the compounds lacking full CHN analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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