Preparation, Characterization and Reactions of Novel Vicinal Dibenzotriazol-1-yl Derivatives of Benzotriazole and Glyoxal [1]

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A variety of novel 1,2-disubstituted-1,2-di(benzotriazol-1-yl)ethane and 1,2-di(benzotriazol-1-yl)ethylene derivatives were prepared from the adduct of benzotriazole and glyoxal.

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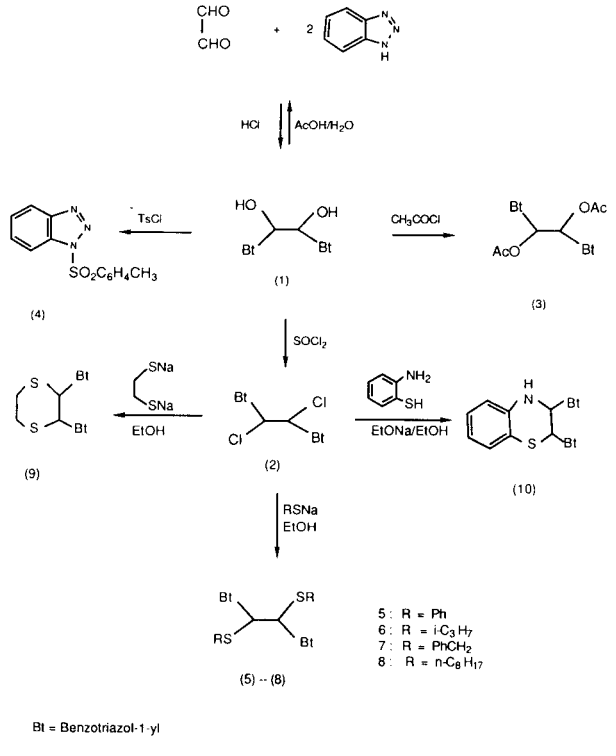
N-Chloromethylheterocycles and *N*-hydroxymethylheterocycles are important intermediates both in synthetic and in industrial chemistry, since the chlorine atom is replaceable by nucleophiles and the *N*-hydroxymethyl group can be condensed with a variety of compounds. Recent work in our laboratory has already shown the versatility of 1-(chloromethyl)- and 1-(hydroxymethyl)benzotriazole as synthetic intermediates [2]. The replacement of the chlorine atom of 1-(chloromethyl)benzotriazole by nucleophiles has received much attention [3-5]. The vicinal dibenzotriazole analogues **1** and **2** and their reactions with nucleophiles, however, have not previously been reported. The present paper describes the preparation, characterization and reactions of a variety of novel vicinal dibenzotriazol-1-yl derivatives of 1,2-di(benzotriazol-1-yl)ethane-1,2-diol (**1**) and of 1,2-dichloro-1,2-di(benzotriazol-1-yl)ethane (**2**).

Results and Discussion.

Glyoxal reacted readily with two equivalents of benzotriazole in aqueous acetic acid to give 1,2-di(benzotriazol-1-yl)ethane-1,2-diol (**1**) in almost quantitative yield. Two signals for each carbon in the ^{13}C nmr and two different CH singlets in the ^{1}H nmr clearly indicated the formation of both the *meso*- and *dl*-diastereoisomers of **1**. Diastereoisomer assignment was achieved by using the chiral shift reagent, tri[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III); the singlet at δ 6.95 ppm split into two broad peaks after the addition of the chiral shift reagent, while that at δ 7.00 ppm remained a singlet shifted slightly down-field. Therefore the signal at δ 6.95 ppm was that of the *dl*-form and that at δ 7.00 represented the *meso*-form. The ratio of the *meso*- to the *dl*-form was 3:1 according to the integrals of the two aliphatic CH signals.

1,2-Di(benzotriazol-1-yl)ethane-1,2-diol (**1**) is stable in water and in organic solvents, but is hydrolyzed to the starting benzotriazole and glyoxal on treatment with aqueous hydrochloric or hydrobromic acid. Bisacylation of diol **1** with acetyl chloride afforded the bisacylated derivative 1,2-di(benzotriazol-1-yl)ethane-1,2-diacetate (**3**) in 54% yield (Scheme 1). This diacetyl derivative **3** was characterized analytically and by its ^{1}H and ^{13}C nmr spectra. The two proton aliphatic CH singlet was shifted from 7.00 ppm in diol **1** to 8.30 ppm after acetylation. The carbonyl signal in the ^{13}C nmr spectrum appeared at 167.6 ppm, aliphatic CH at 75.8 ppm and methyl at 19.5 ppm. Attempted bis-sulfonylation of diol (**1**) with *p*-toluenesulfonyl chloride failed, instead 1-(*p*-toluenesulfonyl)benzotriazole (**4**) was formed in 35% yield along with benzotriazole.

Scheme 1



1,2-Dichloro-1,2-di(benzotriazol-1-yl)ethane (**2**) was prepared in 90% yield by the reaction of **1** with a large excess of thionyl chloride (Scheme 1), in an analogous way to the preparation of 1-(chloromethyl)benzotriazole [2]. Based on its ^{13}C and ^{1}H nmr spectra, the diastereoisomers of **2** could not be distinguished. The aliphatic CH signal appeared at δ 8.58 ppm as a sharp singlet in the ^{1}H nmr and at δ 69.2 ppm in the ^{13}C nmr spectra. The protons of the benzotriazole ring in the ^{1}H spectrum nmr were characteristic: two doublets (8.50 and 8.21 ppm) and two triplets (7.77 and

7.58 ppm), as expected for the 1-substituted benzotriazole derivative.

Previous work has shown that the chlorine atom of 1-(chloromethyl)benzotriazole is readily replaced by a wide range of carbon, nitrogen, phosphorus, oxygen and sulfur nucleophiles to afford substituted products [3-5]. We now report the reaction of 1,2-dichloro-1,2-di(benzotriazol-1-yl)-ethane (**2**) with various nucleophiles. As expected, 1,2-dichloro-1,2-di(benzotriazol-1-yl)ethane (**2**) possessed additional properties because of the presence of the acidic protons of two methine groups. Two competitive pathways, substitution and elimination, occur upon treatment of **2**, with nucleophiles, and we have examined the effects of the nature of the nucleophile and of the reaction conditions on these two competitive reactions.

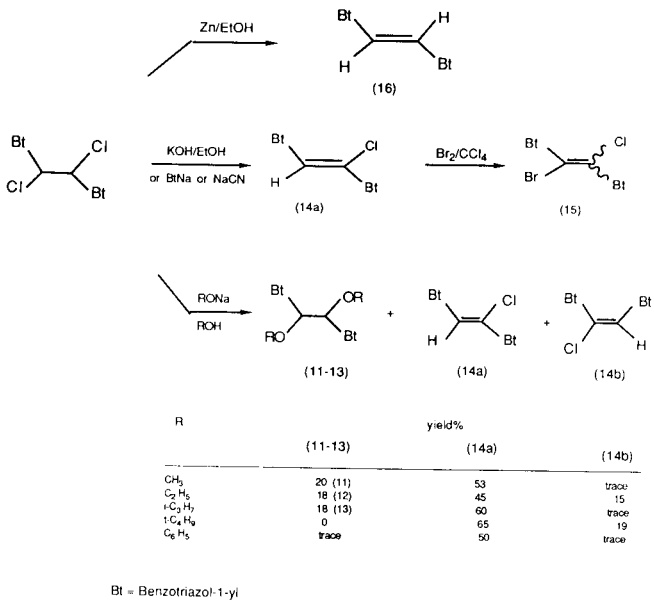
Sulfur nucleophiles reacted readily with 1,2-dichloro-1,2-di(benzotriazol-1-yl)ethane (**2**) to give the expected substituted products. Thus, 1,2-di(phenylthio)-, 1,2-di(isopropylthio)-, 1,2-di(benzylthio)- and 1,2-di(octylthio)-1,2-di-(benzotriazol-1-yl)ethane, **5**, **6**, **7** and **8**, were prepared in high yields by reactions of **2** with sodium thiophenolate, sodium isopropylsulfide, sodium benzylsulfide and sodium octylsulfide, respectively, in ethanol (Scheme 1). In no case was the elimination product detected, which is reasonable since sodium alkylsulfides are strong nucleophiles of weak basicity. The ^1H and ^{13}C nmr spectra of these 1,2-di(alkylthio)-1,2-di(benzotriazol-1-yl)ethanes agreed well with their structures (see Experimental). For compound **7**, the benzyl methylene group appeared as an AB system in its ^1H nmr spectrum. 1,2-Di(isopropylthio)-1,2-di(benzotriazol-1-yl)-ethane (**6**) was formed as a mixture of the two diastereoisomers in about 9:1 ratio, for **5**, **7** and **8**, however, only a single isomer was separated. Unlike *N*-aminoalkylbenzotriazolyl derivatives, which generally exist in solution as mixtures of 1-benzotriazolyl and 2-benzotriazolyl isomers [6-7], the bis *N*-thioalkylbenzotriazoles were all observed only in the 1-benzotriazolyl form.

With sulfur bisnucleophiles the expected heterocycles were produced. Thus the reaction of 1,2-ethanedithiol bissodium salt with **2** in ethanol gave 2,3-di(benzotriazol-1-yl)-1,4-dithiin (**9**) in 80% yield, which showed an AA'BB' pattern in its ^1H nmr spectrum for two methylene groups. Similarly, 2,3-di(benzotriazolyl)benzo-1,4-thiazine (**10**) was obtained from *o*-aminothiophenol and **2** in 90% yield. Both the ^1H and ^{13}C nmr spectra of **10**, however, were very complicated, indicating the existence of 1-benzotriazolyl and 2-benzotriazolyl isomers. The benzotriazole moiety could not be removed from either **9** or **10** by reduction with sodium borohydride.

The reactions of dichloride (**2**) with amines are complex and form mixtures. The 1,2-di(alkylamino)-1,2-di(benzotriazolyl)ethanes have already been prepared by an alternative direct method, the double Mannich condensation of benzotriazole, glyoxal and an amine [7].

With oxygen nucleophiles, elimination reactions are the predominant or exclusive pathway. Sodium methoxide, ethoxide and isopropoxide reacted with 1,2-dichloro-1,2-di(benzotriazol-1-yl)ethane (**2**) to give 1-chloro-1,2-di(benzotriazol-1-yl)ethylene (**14**) as the major product and 1,2-dimethoxy-1,2-di(benzotriazol-1-yl)ethane (**11**), 1,2-diethoxy-1,2-di(benzotriazol-1-yl)ethane (**12**) and 1,2-di(isopropoxy)-1,2-di(benzotriazol-1-yl)ethane (**13**) respectively as the minor products (Scheme 2). Based on the ^1H nmr spectra, compounds **11**, **12** and **13** were produced both in *meso*- and *dl*-forms. With sodium *t*-butoxide or sodium phenoxide, however, only the elimination product **14** was obtained, and no substitution was observed even at low temperature. In the case of sodium ethoxide and *t*-butoxide, the *Z*- and *E*-isomers, **14a** and **14b**, were separated by column chromatography. Both **14a** and **14b** have fourteen signals in the ^{13}C nmr spectra which agree well with the expected structure. The assignment of the stereochemistry is tentative, based on their relative yields and on the chemical shifts of the CH signal [7.98 ppm for **14a** and 8.56 ppm for **14b**], since the CH= signal in the *E*-isomer should receive a down-field chemical shift because of the electron-withdrawing field-effect of the chlorine atom.

Scheme 2



R	yield% (11-13)	(14a)	(14b)
CH_3	20 (11)	53	trace
C_2H_5	18 (12)	45	15
$i\text{-}C_3H_7$	18 (13)	60	trace
$t\text{-}C_4H_9$	0	65	19
C_6H_5	trace	50	trace

Bt = Benzotriazol-1-yl

1-Chloro-1,2-di(benzotriazol-1-yl)ethylene (**14**) was also formed by treatment of dichloride **2** with a variety of other nucleophiles, such as aqueous sodium hydroxide, sodium cyanide in dimethyl sulfoxide, and sodium benzotriazolate in dimethylformamide or in benzene under phase transfer conditions.

Bromination of 1-chloro-1,2-di(benzotriazol-1-yl)ethylene (**14a**) with bromine in carbon tetrachloride afforded

1-chloro-2-bromo-1,2-di(benzotriazol-1-yl)ethylene (**15**) instead of the expected addition product (Scheme 2), presumably the steric hindrance in the addition product destabilized it relative to the olefin. The structure of **15** was confirmed by its elemental analysis. Further elimination of hydrogen chloride from 1-chloro-1,2-di(benzotriazol-1-yl)-ethylene (**14**) to obtain 1,2-dibenzotriazolylacetylene using potassium *t*-butoxide in *t*-butyl alcohol was unsuccessful, the starting material was recovered.

1,2-Dichloro-1,2-di(benzotriazol-1-yl)ethane (**2**) underwent eliminative dechlorination upon treatment with zinc dust in ethanol to give 1,2-di(benzotriazol-1-yl)ethylene (**16**) in 45% yield. Here the two benzotriazole rings are identical both in ^1H and in ^{13}C nmr spectra. The acyclic protons appeared slightly down field at 8.82 ppm and the acyclic carbon signal at 116.3 ppm. Since only a single geometric isomer was obtained, it was reasonably assigned the *trans* structure, and this was supported by its ir spectrum, in which the ν_{CH} was recorded at 1030 cm^{-1}.

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover Capillary melting point apparatus without correction. The ^1H (300 MHz) and ^{13}C nmr spectra were obtained on a Varian VXR-300 (FT mode) spectrometer. Tetramethylsilane was used as the internal standard for the ^1H nmr spectra. Ir spectra were recorded on a Perkin-Elmer 1600 (FTIR) spectrophotometer. Elemental analyses were carried out at the University of Florida and at Hangzhou University on Carlo Erba 1106 instruments.

1,2-Di(benzotriazol-1-yl)ethane-1,2-diol (**1**).

A mixture of benzotriazole (23.8 g, 0.2 mole), glyoxal (5.8 g, 0.1 mole, 40% aqueous solution) and acetic acid (100 ml) in water (300 ml) was allowed to stand overnight at 20°. The resulting precipitate was collected by filtration and washed with water. Drying in a vacuum oven (60°) gave **1** as a white solid (28.5 g, 96%), mp 196-199°; ^1H nmr (dimethyl sulfoxide-d_6): δ 7.70-8.12 (m, 4H), 7.28-7.60 (m, 4H), 7.00 and 6.95 (2s, 2H, CH, ratio: 3:1), 3.60 (br, 2H, OH); ^{13}C nmr: *meso*-form: 145.6, 132.2, 127.3, 124.0, 119.1, 111.3, 82.5 (CHOH); *dl*-form: 145.2, 131.8, 127.1, 123.8, 118.9, 111.5, 83.3 (CHOH).

Anal. Calcd for $C_{14}H_{12}N_6O_2$: C, 56.87; H, 4.19; N, 27.95. Found: C, 56.76; H, 4.05; N, 28.38.

1,2-Dichloro-1,2-di(benzotriazol-1-yl)ethane (**2**).

Thionyl chloride (100 ml) was added dropwise to 1,2-di(benzotriazol-1-yl)ethane-1,2-diol **1** (29.6 g, 0.1 mole) at 20°. The mixture was stirred and refluxed for 3 hours after completion of the addition. Excess thionyl chloride was removed by distillation. Methanol (200 ml) was added and the mixture refluxed for 10 minutes. Cooling and filtration afforded **2** as a white solid (30 g, 90%), mp 188-189°; ^1H nmr (dimethyl sulfoxide-d_6): δ 8.58 (s, 2H, CH), 8.50 (d, J = 8 Hz, 2H), 8.21 (d, J = 8 Hz, 2H), 7.77 (t, J = 8 Hz, 2H), 7.58 (t, J = 8 Hz, 2H); ^{13}C nmr: δ 145.2, 132.4, 128.9, 125.1, 120.0, 111.0, 69.2 (CH).

Anal. Calcd. for $C_{14}H_{10}N_6Cl_2$: C, 50.45; H, 2.80; N, 25.02. Found: C, 50.03; H, 2.80; N, 25.22.

1,2-Diacetoxy-1,2-di(benzotriazol-1-yl)ethane (**3**).

Acetyl chloride (0.8 g, 10 mmoles) was added dropwise to a solution of **1** (1.48 g, 5 mmoles) in benzene (30 ml) and pyridine (1 ml) at 20°. The mixture was stirred for 1 hour at room temperature. The solution was diluted with chloroform (50 ml) and washed with water (20 ml), 10% sodium hydroxide (20 ml) and again water (30 ml). It was dried over potassium carbonate and the solvent removed to give the crude product which was recrystallized from ethanol to give **3** (1.0 g, 54%), mp 228-230°; ^1H nmr (chloroform-d/dimethyl sulfoxide-d_6): δ 8.30 (s, 2H, CH), 8.12 (d, J = 8 Hz, 2H), 8.06 (d, J = 8 Hz, 2H), 7.69 (t, J = 8 Hz, 2H), 7.52 (d, J = 8 Hz, 2H), 1.87 (s, 6H, CH_3); ^{13}C nmr: δ 167.6 (CO), 144.9, 132.4, 128.5, 124.6, 119.4, 110.2, 75.8 (CH), 19.5 (CH_3).

Anal. Calcd. for $C_{18}H_{16}N_6O_4$: C, 56.84; H, 4.24; N, 22.09. Found: C, 57.06; H, 4.38; N, 21.87.

1-(*p*-Toluenesulfonyl)benzotriazole (**4**).

By the above method from *p*-toluenesulfonyl chloride was obtained **4** as white prisms, mp 134-135°; ^1H nmr (chloroform-d): δ 8.12 (d, 1H), 8.06 (d, 1H), 8.00 (d, 2H), 7.66 (t, 1H), 7.48 (t, 1H), 7.32 (d, 2H) ppm; ^{13}C nmr: δ 146.6, 145.2, 133.6, 131.3, 130.1, 130.0, 127.7, 125.7, 120.2, 111.8 ppm.

Anal. Calcd. for $C_{13}H_{11}N_3O_2S$: C, 56.70; H, 4.00; N, 15.87. Found: C, 57.11; H, 4.02; N, 15.50.

1,2-Di(phenylthio)-1,2-di(benzotriazol-1-yl)ethane (**5**).

Sodium metal (0.50 g, 21 mmoles) was added to a solution of thiophenol (2.20 g, 20 mmoles) in methanol (30 ml). On complete dissolution of the metal, 1,2-dichloro-1,2-di(benzotriazol-1-yl)-ethane (3.33 g, 10 mmoles) was added in small portions. The solution was stirred overnight at 25°. The solvent was removed by distillation under reduced pressure and the residue was stirred with water and then filtered. The solid was recrystallized from ethanol to give white needles (4.16 g, 86%) mp 171-173°; ^1H nmr (chloroform-d): δ 8.10 (d, 2H), 6.88-7.50 (m, 18H) ppm: ^{13}C nmr: δ 146.0, 134.6, 132.6, 129.5, 129.2, 128.9, 128.0, 124.4, 120.3, 109.8, 69.0 (CH) ppm.

Anal. Calcd. for $C_{26}H_{20}N_6S_2$: C, 65.00; H, 4.17; N, 17.50. Found: C, 64.65; H, 4.23; N, 17.13.

1,2-Di(isopropylthio)-1,2-di(benzotriazol-1-yl)ethane (**6**).

Compound **6** was prepared as above, 82%, mp 151-154°; ^1H nmr (chloroform-d): δ 8.01 (s, 2H, 2 × CH), 8.00-7.86 (m, 2H), 7.40-7.20 (m, 6H), 2.79 (hept, 2H, 2 × C*H*Me_2), 1.28 (d, 12H, 4 × CH_3) ppm; ^{13}C nmr: δ *major isomer*: 144.7, 132.0, 128.5, 124.5, 120.1, 108.7, 66.1 (CH), 36.7, 22.5 ppm; *minor*: 145.4, 131.3, 128.6, 125.1, 119.7, 109.7, 65.8, 36.2, 22.7 ppm.

Anal. Calcd. for $C_{20}H_{24}N_6S_2$: C, 58.25; H, 5.83; N, 20.39. Found: C, 57.91; H, 6.04; N, 19.97.

1,2-Di(benzylthio)-1,2-di(benzotriazol-1-yl)ethane (**7**).

Compound **7** was prepared as above, white needles (ethanol), 87%, mp 182-184°; ^1H nmr (chloroform-d): δ 8.06 (d, J = 8 Hz, 2H), 7.42-7.28 (m, 4H), 7.20-7.06 (m, 8H), 6.93 (d, J = 7 Hz, 4H), 6.50 (s, 2H, CH), 3.41, 3.28 (AB system, J = 14 Hz, 4H, CH_2) ppm; ^{13}C nmr: δ 146.5, 135.1, 131.6, 128.8, 128.5, 127.7, 127.5, 124.3, 120.1, 110.4, 64.8 (CH), 35.6 (CH_2) ppm.

Anal. Calcd. for $C_{28}H_{24}N_6S_2$: C, 66.14; H, 4.72; N, 16.54. Found: C, 66.02; H, 4.95; N, 16.28.

1,2-Di(*n*-octylthio)-1,2-di(benzotriazol-1-yl)ethane (**8**).

Compound **8** was prepared as above, white needles (ethanol),

72%, mp 91-92°; ^{1}H nmr (chloroform-d): δ 8.12 (d, J = 8 Hz, 2H), 7.75 (d, J = 8 Hz, 2H), 7.50 (t, 2H), 7.42 (t, 2H), 6.79 (s, 2H, CH), 2.28 (m, 4H, SCH_2), 1.32-1.00 (m, 24H), 0.83 (t, J = 7 Hz, 6H, CH_3) ppm; ^{13}C nmr: δ 146.7, 131.7, 127.8, 124.5, 120.4, 110.7, 66.4 (CH), 31.7, 31.5, 28.8, 28.7, 28.4, 28.1, 22.5, 13.9 (CH_3) ppm.

Anal. Calcd. for $C_{30}H_{44}N_6S_2$: C, 65.18; H, 8.02; N, 15.20. Found: C, 65.01; H, 8.33; N, 14.90.

2,3-Di(benzotriazol-1-yl)-1,4-dithiin (**9**).

Sodium metal (0.50 g, 21 mmoles) was added to a solution of ethanedithiol (0.62 g, 10 mmoles) in ethanol (30 ml). After complete dissolution of the sodium, 1,2-dichloro-1,2-di(benzotriazol-1-yl)ethane (3.33 g, 10 mmoles) was added in one portion, the mixture stirred at 30° for 6 hours and poured in water (100 ml). The resulting solid was collected and recrystallized from ethanol to give white needles (80%), mp 232-235°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 7.79 (d, 2H), 7.10 (t, 2H), 7.00 (t, 2H), 6.95 (s, 2H, CH), 6.66 (d, 2H), 3.98 (q, 2H), 3.46 (q, 2H) ppm; ^{13}C nmr: δ 144.3, 132.3, 126.8, 123.4, 118.8, 108.3, 58.4 (CH), 29.4 (CH_2) ppm.

Anal. Calcd. for $C_{16}H_{14}N_6S_2$: C, 54.22; H, 3.98; N, 23.71. Found: C, 54.60; H, 4.12; N, 23.41.

2,3-Dihydro-2,3-di(benzotriazol-1-yl)benzo-1,4-thiazine (**10**).

Compound **10** was prepared as above from **2** and *o*-aminothiophenol, pale yellow plates (90%), mp 139-141°; ^{1}H nmr (dimethylsulfoxide-d_6): δ 8.10-6.15 (m, 14H), 4.00 (br, 1H, NH).

Anal. Calcd. for $C_{20}H_{15}N_7S$: C, 62.40; H, 3.88; N, 26.07. Found: C, 62.34; H, 3.90; N, 25.55.

1,2-Dimethoxy-1,2-di(benzotriazol-1-yl)ethane (**11**).

This compound was prepared as described for **13**, mp 108-111°; ^{1}H nmr (chloroform-d): δ 8.05-7.80 (m, 2H), 7.55-7.25 (m, 6H), 7.10 and 7.05 (s, 2H, CH), 4.20 and 3.76 (s, 6H, 2 × OCH_3, ratio = 2:1) ppm; ^{13}C nmr: δ 145.1, 144.8, 133.9, 133.7, 129.5, 125.0, 124.9, 120.8, 120.6, 109.8, 109.5, 96.6 (CH), 50.8 (OCH_3) ppm.

Anal. Calcd. for $C_{16}H_{16}N_6O_2$: C, 59.26; H, 4.94; N, 25.93. Found: C, 59.65; H, 5.07; N, 25.55.

1,2-Diethoxy-1,2-di(benzotriazol-1-yl)ethane (**12**).

Compound **12** was prepared as described for **13**, mp 130-132°; ^{1}H nmr (chloroform-d): δ 8.50-8.00 (m, 4H), 7.85-7.38 (m, 6H), 4.60 and 4.20 (q, 4H, ratio = 2:1 OCH_2); 1.77 and 1.46 (t, 6H, ratio = 2:1 CH_3) ppm; ^{13}C nmr: δ 144.9, 144.7, 133.8, 133.7, 129.7, 129.5, 125.0, 124.9, 119.8, 119.6, 110.0, 109.8, 96.0 (CH), 57.0, 16.7, 16.5 ppm.

Anal. Calcd. for $C_{18}H_{20}N_6O_2$: C, 61.36; H, 5.68; N, 23.86. Found: C, 60.98; H, 5.81; N, 23.52.

1,2-Di(isopropoxy)-1,2-di(benzotriazol-1-yl)ethane (**13**).

To a solution of sodium (0.23 g, 10 mmoles) in 2-propanol (25 ml) was added 1,2-dichloro-1,2-di(benzotriazol-1-yl)ethane (1.67 g, 5 mmoles). The solution was heated at 40° for 4 hours, cooled to room temperature and the solvent removed under reduced pressure. The residue was dissolved in ether and washed with water. The etheral solution was dried (magnesium sulfate) and concentrated. The expected 1,2-di(isopropoxy)-1,2-di(benzotriazol-1-yl)ethane (**13**) was separated by column chromatography (silica gel, chloroform) as minor product (18%), mp 171-173°; ^{1}H nmr (chloroform-d/dimethyl sulfoxide-d_6): δ 7.72-8.00 (m, 2H), 7.25-7.60 (m, 8H, BtH and CH), 4.68 (hept, 2H, 2 × C*H*Me_2), 1.58 (d, 6H, CH_3) ppm; ^{13}C nmr: δ (*meso*-and *dl*-form) 144.3, 143.9, 132.7, 131.5, 128.6, 127.5, 124.4, 123.7, 119.3, 119.0, 109.9, 109.3, 99.5, 73.9, 21.1 ppm.

Anal. Calcd. for $C_{20}H_{24}N_6O_2$: C, 63.16; H, 6.32; N, 22.11. Found: C, 62.83; H, 6.57; N, 21.90.

Z-1-Chloro-1,2-di(benzotriazol-1-yl)ethylene (**14a**).

This compound was prepared as above using sodium *t*-butoxide in *t*-butyl alcohol as pale yellow plates (62%), mp 134-136°; ^{1}H nmr (chloroform-d): δ 8.00 (d, J = 8 Hz, 1H), 7.97 (s, 1H, CH=), 7.89 (d, J = 8 Hz, 1H), 7.43-7.20 (m, 5H), 7.13 (d, J = 8 Hz, 1H) ppm; ^{13}C nmr: δ 145.2, 144.6, 132.0, 131.5, 129.2, 128.9, 124.9, 124.8, 120.5, 120.3, 119.6, 119.3, 109.3, 108.5 ppm.

Anal. Calcd. for $C_{14}H_9N_6Cl$: C, 56.65; H, 3.04; N, 28.33. Found: C, 56.23; H, 2.95; N, 28.66.

This compound was also prepared by the reactions of 1,2-dichloro-1,2-di(benzotriazol-1-yl)ethane with a variety of bases, such as sodium ethoxide, sodium phenoxide, cyanide, and sodium benzotriazol-1-ate.

E-1-Chloro-1,2-di(benzotriazol-1-yl)ethylene (**14b**).

This product was separted by column chromatography (silica gel, chloroform) as a minor product from the reaction of 1,2-dichloro-1,2-di(benzotriazol-1-yl)ethane with *t*-butoxide (24%), mp 128-129°; ^{1}H nmr (chloroform-d): δ 8.58 (s, 1H, CH=), 8.07 (d, J = 8 Hz, 1H), 7.90 (d, J = 8 Hz, 1H), 7.75 (d, J = 8 Hz, 1H), 7.52-7.30 (m, 5H) ppm; ^{13}C nmr: δ 144.8, 143.8, 131.8, 131.6, 128.9, 128.6, 124.7, 124.6, 120.4 (CH=), 119.7, 119.3, 117.2 (CH=), 109.5 ppm.

Anal. Calcd. for $C_{14}H_9N_6Cl$: C, 56.65; H, 3.04; N, 28.33. Found: C, 56.76; H, 3.04; N, 28.70.

1-Bromo-2-chloro-1,2-di(benzotriazol-1-yl)ethylene (**15**).

Bromine (3.95 g, 25 mmoles) was added dropwise at 25° to 1-chloro-1,2-di(benzotriazol-1-yl)ethylene (10 mmoles) suspended in carbon tetrachloride (20 ml). The mixture was stirred at 25° for 1 hour then at 50° for another 1 hour. After cooling, the resulting solid was collected and washed with water and ethanol. Recrystallization from ethanol gave pale prisms (52%), mp 161-163°; ^{1}H nmr (chloroform-d): δ 8.22 (d, 2H), 7.84 (m, 4H), 7.58 (t, 2H) ppm; ^{13}C nmr: δ 145.5, 145.4, 131.8, 131.6, 129.7, 129.6, 125.4, 120.7, 113.1, 112.0, 110.4, 110.2 ppm.

Anal. Calcd. for $C_{14}H_8N_6BrCl$: C, 44.24; H, 2.01; N, 22.69. Found: C, 44.65; H, 2.13; N, 22.38.

Z-1,2-Di(benzotriazol-1-yl)ethylene (**16**).

1,2-Dichloro-1,2-(benzotriazol-1-yl)ethane (**2**) (1.67 g, 5 mmoles) and zinc dust (1.0 g) were heated under reflux in ethanol for 3 hours. The solid was filtered off and the solvent removed under reduced pressure. The residue was poured into water (50 ml), extracted with chloroform (3 × 20 ml) and dried over magnesium sulfate. Removal of the solvent gave the product (45%), mp >250°; ^{1}H nmr (chloroform-d/dimethyl sulfoxide-d_6): δ 8.82 (s, 2H, CH=), 8.25 (d, 2H), 8.13 (d, 2H), 7.68 (t, 2H), 7.50 (t, 2H) ppm; ^{13}C nmr: δ 145.3, 131.6, 128.3, 124.6, 119.4, 116.3, 110.8 ppm; ir (nujol): ν 1611, 1492, 1458, 1171, 1030, 936 cm^{-1}.

Anal. Calcd. for $C_{14}H_{10}N_6$: C, 64.12; H, 3.82; N, 32.04. Found: C, 63.77; H, 3.72; N, 31.51.

REFERENCES AND NOTES

[1] This paper constitutes a part in our series "The Chemistry of Benzotriazole," see *e.g.*: A. R. Katritzky, L. Urogdi, and A. Mayence, *J.*

Chem. Soc., Chem. Commun., 337 (1989); A. R. Katritzky and C. V. Hughes, *Chem. Scr.*, **29**, 27 (1989).

[2] J. H. Burckhalter, V. C. Stephens and L. A. R. Hall, *J. Am. Chem. Soc.*, **74**, 3868 (1952).

[3] P. Baumann, German Offen. 2,357,910; *Chem. Abstr.*, **81**, 105521 (1974).

[4] A. R. Katritzky, S. Rachwal, K. C. Caster, F. Mahni, K. W. Law and O. Rubio, *J. Chem. Soc., Perkin Trans 1*, 781 (1987).

[5] A. R. Katritzky and M. Drewniak, *Tetrahedron Letters*, **29**, 1755 (1988).

[6] J. R. S. Lindsay, and J. S. Sadd, *J. Chem. Soc., Perkin Trans. 2*, 741 (1976).

[7] A. R. Katritzky and W. Q. Fan, *J. Org. Chem.*, **55**, 3205 (1990).