N-Substituted Benzotriazoles as Synthons for 1,3-Dipoles

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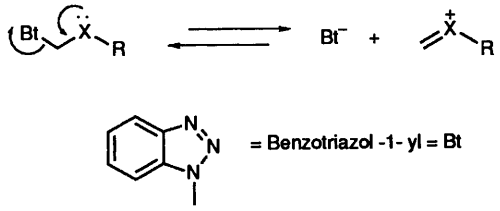
N-Bis(benzotriazol-1-ylmethyl)hydroxylamine has been shown to be an effective synthon for the nitrone 1,3-dipole. Regio- and stereo-specific cycloaddition with several dipolarophiles to furnish substituted 2-(benzotriazol-1-ylmethyl)isoxazolidines is described. Subsequent replacement of the benzotriazole entity is reported, and reaction of the cycloadducts with perchloric acid is shown to yield isoxazolidines without nitrogen substitution. The synthesis of the novel tricyclic ring system 12-oxa-1,3-diazatricyclo[7.2.1.$0^{3,8}$]dodec-5-ene is also reported. Benzotriazol-1-ylmethylene(benzotriazol-1-ylmethyl)amine does not act as a synthon for the azomethine ylide.

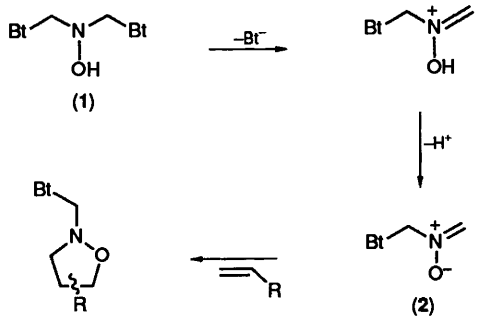
1,3-Dipolar cycloadditions are of the greatest importance for the synthesis of 5-membered heterocyclic compounds.[1-7] The reaction is versatile in regard to the range of heterocycles that may be prepared, generally high yielding, and both regio- and stereo-specific in the vast majority of reported cases. In accord with such desirable characteristics, 1,3-dipolar cycloadditions are finding increasing use in synthetic organic chemistry. New methods by which 1,3-dipoles may be generated, and demonstrating the successful cycloaddition of such species, is of great current interest. The present paper reports our preliminary findings in the use of bis(benzotriazol-1-ylmethyl)amine and bis(benzotriazol-1-ylmethyl)hydroxylamine as sources of 1,3-dipoles.

The use of *N*-substituted benzotriazoles as synthetic intermediates in the preparation of many classes of organic compounds, such as amines, hydroxylamines,[8-10] and amides,[11,12] has been reported previously. Generally such methods have relied on the ease with which benzotriazolate may be displaced by suitable nucleophiles. In particular, when the benzotriazolyl substituent is α to a heteroatom with an available lone pair of electrons (nitrogen or sometimes oxygen), solutions of such adducts frequently exist in equilibrium with their ionised counterparts (Scheme 1).[13,14]



Scheme 1.

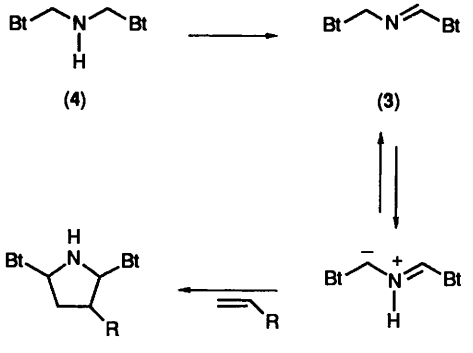
The particularly labile nature of the benzotriazole–carbon bond in compounds of this type prompted us to consider bis(benzotriazol-1-ylmethyl)hydroxylamine (**1**) as a potential synthon for the nitrone 1,3-dipole (Scheme 2). In this compound, the +M effect of the oxygen α to the nitrogen is expected to enhance the leaving tendency of the benzotriazolate anion, and, together with loss of the hydroxy proton, this would result in formation of the intermediate nitrone (**2**). Reactions of this nitrone equivalent with 1,3-dipolarophiles could posses significant advantages over existing methods. The isoxazolidine products formed in this way possess a methylene group at the 3-position. To our knowledge, only a single method for the preparation of such compounds by a cycloaddition route has been demonstrated and this involves the use of reactive methanal with primary hydroxylamines.[15-22] Furthermore, the



Scheme 2.

products retain a *N*-benzotriazolylmethyl substituent which is available for further synthetic manipulation.

The work predominantly of Grigg and co-workers on the 1,3-dipolar cycloadditions of imines,[23-30] also alerted us to the possible use of benzotriazol-1-ylmethylene(benzotriazol-1-ylmethyl)amine (**3**) in similar reactions (Scheme 3). The preparation of this synthon for the azomethine ylide could be envisaged from either bis(benzotriazol-1-ylmethyl)amine (**4**),[31] or the hydroxylamine.[32] Successful cycloaddition of imine (**3**) with ethylenic dipolarophiles, with subsequent elimination of benzotriazole, would ultimately lead to the formation of substituted pyrroles.

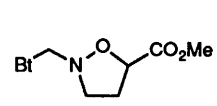


Scheme 3.

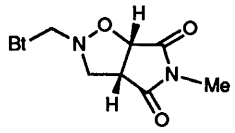
Results and Discussion

Bis(benzotriazol-1-ylmethyl)amine (**4**) and bis(benzotriazol-1-ylmethyl)hydroxylamine (**1**) were prepared by reported methods.[13] We found that the imine (**3**) was easily available from compound (**4**) by oxidation with iodosobenzene.[31]

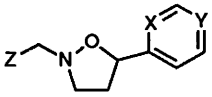
We have confirmed that bis(benzotriazol-1-ylmethyl)-hydroxylamine does indeed react with dipolarophiles to give the expected cycloadducts. Thus, refluxing compound (**1**) in toluene with methyl acrylate, with *N*-methylmaleimide, with 2-vinylpyridine, with 4-vinylpyridine, with acrylonitrile, or with dimethyl fumarate, results in the formation of isoxazolidines [(**5**)–(**10**), respectively]. ^{1}H NMR decoupling experiments show unambiguously that the 5-substituted isoxazolidines (**5**), (**7**), (**8**), and (**9**) are produced regiospecifically in the reaction with monosubstituted alkenes. Similar decoupling experiments, and measurement of the NOE between 3a-H and 6a-H (approximately 10%) of the adduct (**6**) derived from *N*-methylmaleimide, clearly indicate that the addition is stereospecifically *syn*. Such observed specificities support a concerted mechanism of reaction.



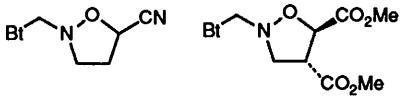
(**5**)



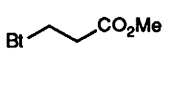
(**6**)



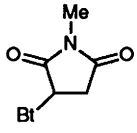
	X	Y	Z
(**7**)	N,	CH,	Bt
(**8**)	CH,	N,	Bt
(**14**)	N,	CH,	H
(**15**)	CH,	N,	H



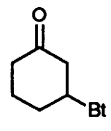
(**9**) (**10**)



(**11**)



(**12**)



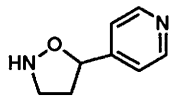
(**13**)

However, the isolation of cycloadducts (**5**) and (**6**) is complicated by a competitive reaction involving the molecule of benzotriazole which is liberated during the course of the ionisation equilibrium. Since dipolarophiles are typically potent Michael acceptors, 1,4-addition of benzotriazole also occurs. Thus, Michael adducts (**11**) and (**12**) were isolated as mixtures of benzotriazol-1-yl and -2-yl isomers, along with the corresponding cycloadducts (**5**) and (**6**), respectively. Although we have been unable to prevent the formation of the Michael adducts, the use of 2 equivalents of dipolarophile results in high yields of the analogous isoxazolidines. In the reactions of 2-vinylpyridine, 4-vinylpyridine, acrylonitrile and *trans*-dimethyl butenedioate to give compounds (**7**), (**8**), (**9**), and (**10**), respectively, concomitant 1,4-addition was not observed provided equimolar quantities of the reactants were employed. Cycloadducts (**5**), (**7**), (**8**), and (**10**) could be isolated efficiently by column chromatography. Compounds (**6**) and (**9**) were purified by recrystallisation.

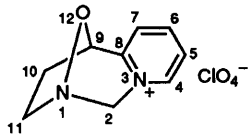
The use of acetylenic dipolarophiles did not result in the formation of cycloadducts. Indeed, no pure products were isolated from the reaction of compound (**1**) with either dimethyl butynedioate or phenylethyne. No reaction was observed with styrene as the dipolarophile, whereas the use of cyclohex-2-enone resulted only in the formation of a small quantity of the Michael adduct (**13**).

Methods for the displacement of the benzotriazolyl entity from a wide range of compounds have already been reported.[8,9,33] To demonstrate similar removal of benzotriazolate from the product isoxazolidines, cycloadducts (**7**) and (**8**) were treated with a small molar excess of sodium borohydride in ethanol. 2-Methyl-5-(2-pyridyl)isoxazolidine (**14**) and 2-methyl-5-(4-pyridyl)isoxazolidine (**15**) were obtained in 59 and 68% yield, respectively. Strangely, we were unable to obtain well resolved ^{1}H NMR spectra for these compounds, whereas the carbon resonances in the ^{13}C NMR spectrum were observed as close doublets of differing intensity. These effects are believed to be caused by a relatively slow inversion of the isoxazolidine nitrogen, allowing observation of both stereoisomers in the NMR spectra.[34] That the nitrogen inversion of *N*-methylisoxazolidines is slow on the NMR time scale has previously been demonstrated.[35–37] An analogous lack of resolution was not observed in the NMR spectra of the cycloadducts (**7**) and (**8**). Recording the ^{1}H NMR of the isoxazolidine (**15**) at elevated temperature resulted in increased resolution and signal intensity, whereas coalescence of the doublets was observed in the ^{13}C NMR spectrum. The purities of the samples of the isoxazolidines (**14**) and (**15**) were confirmed by GLC, and the compounds were characterised by high resolution mass spectrometry and by conversion into dipicrates.

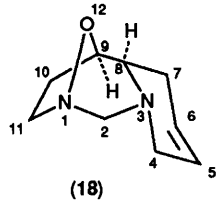
The removal of tetrahydropyran (THP) from 2-tetrahydropyran-2-ylisoxazolidines by the action of perchloric acid has recently been reported.[21] This method, which provides a route to isoxazolidines without nitrogen substitution, is a rare cycloaddition route to such compounds.[38–42] Noting the similarity between the (THP) group and the benzotriazol-1-ylmethyl substituent, analogous reactions were undertaken with the cycloadducts (**7**) and (**8**). In the latter case, reflux for 15 min with a 1.1 molar excess of 70% perchloric acid in ethanol yielded 5-(4-pyridyl)isoxazolidine (**16**) in good yield. The reaction of (**7**) under analogous conditions yielded the perchlorate salt of the bridged pyridinium compound (**17**). To our knowledge, this is the first reported synthesis of the 12-oxa-1,3-diazatricyclo[7.2.1.0^{3,8}]dodeca-3,5,7-trien-3-ium perchlorate framework. ^{1}H and ^{13}C NMR spectra are entirely consistent with the assigned tricyclic structure. In the ^{1}H NMR spectrum of (**17**) seven proton resonances are observed in the alkyl region, and four in the aromatic region. In the ^{13}C NMR



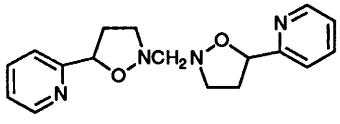
(**16**)



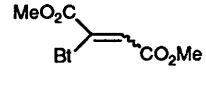
(**17**)



(**18**)



(**19**)



(**20**)

spectrum four carbon resonances are observed in the alkyl region (three methylene, and one methyne are evident in DEPT spectra), and five in the aromatic region (four proton bearing and one quaternary). The chemical shifts of these resonances are

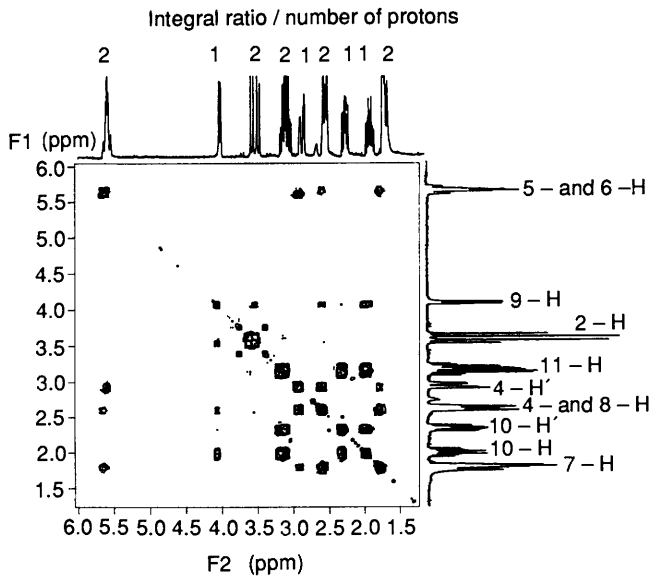


Figure 1. 2D Proton–proton COSY spectrum of 12-oxa-1,3-diaza-tricyclo[7.2.1.$0^{3,8}$]dodec-5-ene.

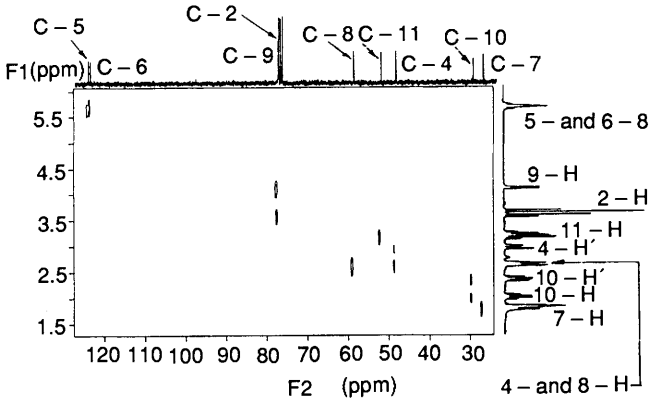


Figure 2. 2D Proton–carbon HETCOR spectrum of 12-oxa-1,3-diaza-tricyclo[7.2.1.$0^{3,8}$]dodec-5-ene

in accord with the proposed structure. The protons of the methylene bridge between the two nitrogen atoms are magnetically non-equivalent and appear as a pair of gem-coupled doublets (^2J = 14.0 Hz) at 5.53 and 5.98 ppm. The increased separation of the chemical shift for each proton resonance, relative to those observed in (**7**) for the NCH_2N methylene (5.78 and 5.84 ppm), being indicative of the greater rigidity of the tricyclic system. The carbon resonance of this same methylene is also found at lower field (76.24 ppm), relative to that of (**7**) (67.13 ppm), due to deshielding by the adjacent pyridinium nitrogen. The average value of the chemical shifts of the pyridine proton and carbon resonances for (**17**) are also significantly shifted to lower field relative to those of (**7**). Selective decoupling of the proton resonances observed in the ^1H NMR spectrum indicates that coupling is present between all geminal and vicinal protons in accord with those expected for (**17**). The observation of a large NOE effect between 2-H and 4-H (16%), and a significantly smaller effect between 2-H′ and 4-H (6%), is strong evidence in support of the bridged structure with its conformational rigidity at C-2. As expected, a large NOE effect is present between 9-H and 7-H (15%). Elemental analysis of the salt agrees with the molecular formula of (**17**).

Reaction of (**17**) with 1 molar equiv. of $NaBH_4$ in ethanol results in partial reduction of the pyridine ring. ^1H and ^{13}C NMR spectra are consistent with the presence of a single double bond remaining in the molecule. The ^{13}C NMR spectrum of the product clearly shows that the reduction is diastereospecific, and that only a single regioisomer is formed. The two-dimensional COSY and HETCOR spectra of this product are shown in Figures 1 and 2, respectively. Strong coupling is observed between the alkenyl protons and the protons of two methylenes, and this allows the identification of the product as 12-oxa-1,3-diazatricyclo[7.2.1.$0^{3,8}$]dodec-5-ene (**18**). The observation of NOE effects between 7-H and 10-H′ (4%), and between 4-H′ and 11-H (13%), clearly indicate a *trans* relationship between 8-H and 9-H, and thus unambiguously assigns *endo* stereochemistry to the diastereoisomer.

Increasing the reaction time of (**7**) with the perchloric acid resulted in formation of what appears to be the dimeric product (**19**).

The reaction of benzotriazol-1-ylmethylene(benzotriazol-1-ylmethyl)amine (**3**) with dipolarophiles did not result in the formation of cycloadducts. No reaction was observed upon reflux of (**3**) in toluene or xylene with either methyl acrylate, *N*-methylmaleimide, or dimethyl butynedioate. Addition of 1 equiv. of trifluoroacetic acid to the reactants[29] with subsequent reflux in toluene results in high yields of the 1,4-addition products (**11**), (**12**), and (**20**), respectively. Moreover, the yields of these adducts approach 2 mol equiv. of the reagent imine, indicating extensive decomposition of (**3**) under the reaction conditions employed.

The failure of (**3**) to undergo 1,3-dipolar cycloaddition, in a manner analogous to previously reported systems, can be explained by the relatively low acidity of the methylene protons. In all cases of successful cyclisation, prototropic tautomerism of the imine to the reactive azomethine ylide has been aided by the presence of strongly electron-withdrawing substituents at the potential carbanionic site.[23–30] Although benzotriazole has indeed been shown to stabilise such negative charges, its effect is not sufficient to induce appreciable tautomerisation of the imine.

We are currently further investigating the use of other *N*-substituted benzotriazoles, as synthetic auxiliaries in a variety of cyclisations.

Experimental

M.p.s were determined on a Fisher-Johns hot-stage melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian XL300 spectrometer (300 and 75 MHz, respectively), using $CDCl_3$ as solvent (unless otherwise stated) and tetramethylsilane as an internal reference. ^1H and ^{13}C NMR chemical shifts are reported in ppm (δ). For each carbon value the number of attached hydrogen atoms (DEPT pulse sequence) is reported in parentheses immediately after the chemical shift. High resolution and electron impact source mass spectra were recorded on a Kratos AEI MS 30 with a Data General Nova data system. Where stated, chemical ionisation (CH_4) mass spectra were recorded on a Finnigan 4500 quadrupole mass spectrometer. IR spectra were recorded as neat samples (unless otherwise stated) on a Perkin-Elmer 1600 series FTIR and absorbances are reported in wavenumbers. Elemental analyses were performed on a Carlo Erba 1106 elemental analyser. Commercially available reagent grade solvents were thoroughly dried in accord with standard methods prior to use. Preparative chromatography was performed by flash column chromatography with silica gel (EM Merck 60, 230–400 mesh) or by the use of a radial, centrifugally accelerated thin layer chromatograph ('Chromatatron', Harrison Research, Palo Alto, California).

Benzotriazol-1-ylmethylene(ber otriazol-1-ylmethyl)amine (**3**).—Bis(benzotriazol-1-ylmethyl)amine (**4**) (0.2 g, 7.20 × 10^{-4}

mol) was suspended in dry CH_2Cl_2 (20 ml) and stirred at room temperature under N_2. Iodosobenzene (0.32, 1.43 × 10^{-3} mol) was then added, together with 4 Å molecular sieves (0.5 g). The mixture was stirred for 16 h, filtered, and the solvent evaporated under reduced pressure. The major product was purified by flash chromatography using $CHCl_3$ as eluant; yield 0.11 g (61%), m.p. 197–198 °C; δ_H 6.56 (2 H, d, 1.5 Hz, CH_2), 7.26–7.67 (5 H, m, BtH), 8.10 (1 H, d, 7.3 Hz, BtH), 8.16 (1 H, d, 7.3 Hz, BtH), 8.25 (1 H, d, 8.2 Hz, BtH), and 8.93 (1 H, t, 1.5 Hz, HC=N); δ_C 65.63 (2, CH_2), 109.23, 114.20, 120.12, 120.53, 124.55, 126.20, 128.35, 129.82 (1, Bt C-4, -5, -6, and -7), 132.84, 133.16, 146.4, 146.64 (0, Bt C-3a and -7a), and 147.84 (1, N=CH); *m/z* (self-condenses; molecular ion observed only at very low concentrations) 277 (M^+, 1%), 248 (2), 220 (8), 132 (18), 130 (30), 119 (18), 104 (22), 91 (32), and 77 (100); ν_{max}(Nujol) 1 608 (w, C=N) (Found: C, 60.75; H, 3.95; N, 36.1. $C_{14}H_{11}N_7$ requires 60.64; H, 4.00; N, 35.36%; the value for N was consistently found to be high).

Methyl 2-(*Benzotriazol*-1-*ylmethyl*)*isoxazolidine*-5-*carboxylate* (**5**).—The hydroxylamine (**1**) (0.2 g, 6.8 × 10^{-4} mol) was suspended in toluene (5 ml). Methyl acrylate (0.11 g, 1.4 × 10^{-4} mol) was added and the mixture heated under reflux for 16 h. The solvent was removed under reduced pressure. The crude product oil was separated into its components by flash chromatography using $CHCl_3$ as eluant. In order of elution. 1, mixture of methyl 3-benzotriazol-1-yl- and 3-benzotriazol-2-yl-propanoate (oil) (**11**) (0.14 g, 100%); 2, methyl 2-(benzotriazol-1-ylmethyl)isoxazolidine-5-carboxylate (**5**) (0.17 g, 100%), m.p. 73–75 °C (recrystallised from toluene–hexane); δ_H 2.07 (1 H, m, 4-H), 2.32 (1 H, m, 4-H′), 3.13 (1 H, m, 3-H), 3.24 (1 H, m, 3-H′), 4.34 (1 H, dd, 9.0 Hz, 4.5 Hz, 5-H), 5.75 (1 H, d, 14.4 Hz, NC*H*H′N), 5.86 (1 H, d, 14.4 Hz, NCH*H*′*N*), 7.39 and 7.52 (1 H, dd, 8.1 Hz, 8.0 Hz, Bt 5-H and 6-H), 7.80 (1 H, d, 8.0 Hz), and 8.06 (1 H, d, 8.1 Hz, Bt 4-H and 7-H); δ_C 33.04 (2, C-4), 49.28 (2, C-3), 52.39 (3, Me), 66.71 (2, NCH_2N), 75.68 (1, C-5), 111.06, 119.65, 124.21, 127.89 (1, Bt C-4, -5, -6, and -7), 133.99, 145.96 (0, Bt C-3a and -7a), and 171.86 (0, *C*O_2Me); *m/z* 262 (M^+, 2%) 203 (3), 144 (37), 133 (8), 132 (78), 119 (7), 104 (32), 78 (11), and 77 (100); ν_{max}(Nujol) 1 743 (s, CO) (Found: C, 55.02; H, 5.5; N, 21.0. $C_{12}H_{14}N_4O_3$ requires C, 54.96; H, 5.38; N, 21.36%).

cis-2-(*Benzotriazol*-1-*ylmethyl*)-5-*methyl*-2,3,3a,6a-*tetrahydropyrrolo*[3,4-*d*]*isoxazole*-4,6-*dione* (**6**).—The hydroxylamine (**1**) (0.5 g, 1.7 × 10^{-3} mol) was suspended in toluene (10 ml). Methyl acrylate (0.38 g, 3.4 × 10^{-3} mol) was added and the mixture heated under reflux for 24 h. The solution was then cooled to −15 °C for 96 h. The resultant white precipitate was collected at the pump and washed with cold toluene; yield 0.48 g (100%), m.p. 204–205 °C (from aqueous EtOH); δ_H 2.70 (1 H, dd, 10.1 Hz, 8.0 Hz, 3-H), 3.06 (3 H, s, Me), 3.41 (1 H, br t, 7.6 Hz, 3a-H), 3.59 (1 H, d, 10.1 Hz, 3-H′), 4.63 (1 H, d, 7.3 Hz, 6a-H), 5.76 (1 H, d, 15.1 Hz, NC*H*H′N), 5.90 (1 H, d, 15.1 Hz, NCH*H*′N), 7.41 (1 H, dd, 8.6 Hz, 6.3 Hz) and 7.54 (1 H, dd, 8.3 Hz, 6.3 Hz, Bt 5-H and 6-H), 7.77 (1 H, d, 8.6 Hz), and 8.06 (1 H, d, 8.3 Hz, Bt 4-H and 7-H); δ_C 25.20 (3, Me), 48.08 (1, C-3a), 52.27 (1, C-3), 63.40 (2, NCH_2N), 75.65 (1, C-6a), 111.02, 119.68, 124.35, 128.12 (1, Bt C-4, -5, -6, and -7), 133.93, 145.85 (0, Bt C-3a and -7a), 174.25 (0, C-4), and 175.42 (0, C-6); *m/z* 288 (M + 1, 10%), 287 (M^+, 5%), 188 (8), 169 (74), 133 (13), 132 (100), 104 (42), 77 (86), and 55 (27); ν_{max}(Nujol) 1 778w and 1 700s (CO) (Found: C, 54.25; H, 4.6; N, 24.5. $C_{13}H_{13}N_5O_3$ requires C, 54.35; H, 4.56; N, 24.38%).

2-*Benzotriazol*-1-*ylmethyl*)-5-(2-*pyridyl*)*isoxazolidine* (**7**).—The hydroxylamine (**1**) (0.4 g, 1.36 × 10^{-3} mol) was suspended in toluene (10 ml). 2-Vinylpyridine (0.14 g, 1.36 × 10^{-3} mol) was added and the mixture heated under reflux for 30 h. The solvent was removed under reduced pressure and the crude product purified by flash chromatography using Et_2O as eluant, yield 0.32 g (83%); δ_H 2.32 (2 H, br q, 7.1 Hz, 4-H), 3.24 (2 H, td, 9.6 Hz, 2.2 Hz, 3-H), 4.98 (1 H, br t, 9.6 Hz, 5-H), 5.78 (1 H, d, 16.0 Hz, NC*H*H′N), 5.84 (1 H, d, 16.0 Hz, NCH*H*′N), 7.12 (1 H, br dd, 7.3 Hz, 6.0 Hz,), 7.22 (1 H, br d, 7.9 Hz), 7.38 (1 H, br t, 9.0 Hz), 7.47 (1 H, br t, 9.0 Hz) and 7.56 (1 H, td, 7.9 Hz, 1.7 Hz pyridine 3-, 4-, 5-H, Bt 5-H and 6-H), 7.78 and 8.06 (1 H, d, 8.3 Hz, Bt 4-H and 7-H), and 8.47 (1 H, d, 3.9 Hz pyridine 6-H); δ_C 35.56 (2, C-4), 50.08 (2, C-3), 67.13 (2, NCH_2N), 80.16 (1, C-5), 111.02, 119.60, 124.11, 127.72 (1, Bt C-4, -5, -6, and -7), 120.29, 122.46 (1, pyridine C-3 and -5), 133.92, 145.95 (0, Bt C-3a and -7a), 136.61 (1, pyridine C-4), and 160.52 (1, pyridine C-6); *m/z* (chemical impact) 281 (M^+, 14%) and 118 (100) (Found: C, 64.2; H, 5.6; N, 24.8 $C_{15}H_{15}N_5O$ requires C, 64.04; H, 5.37; N, 24.89%).

2-(*Benzoltriazol*-1-*ylmethyl*)-5-(4-*pyridyl*)*isoxazolidine* (**8**).—The hydroxylamine (**1**) (0.20 g, 6.8 × 10^{-4} mol) was suspended in dry toluene (10 ml). 4-Vinylpyridine (0.07 g, 6.8 × 10^{-4} mol) was added and the mixture heated under reflux for 12 h. The solvent was removed under reduced pressure and the major product separated with a Chromatatron using 1:1 $CHCl_3$–EtOAc as eluant; yield 0.154 g (81%), viscous oil); δ_H 1.99 (1 H, septet, 6.5 Hz, 4-H), 2.35 (1 H, m, 4-H′), 3.25 (2 H, m, 3-H), 4.82 (1 H, t, 7.9 Hz, 5-H), 5.82 (1 H, d, 15.0 Hz, NC*H*H′N), 5.83 (1 H, d, 15.0 Hz, NCH*H*′N), 7.04 (2 H, d, 5.8 Hz, pyridine 3-H), 7.41 (1 H, t, 8.2 Hz) and 7.50 (1 H, t, 7.8 Hz, Bt 5-H and 6-H), 7.76 (1 H, d, 8.2 Hz) and 8.06 (1 H, d, 7.8 Hz, Bt 4-H and 7-H), and 8.46 (2 H, d, 5.8 Hz, pyridine 2-H); δ_C 36.96 (2, C-4), 49.74 (2, C-3), 66.60 (2, NCH_2N) 77.87 (1, C-5), 110.96, 119.67, 124.29, 127.89 (1, Bt C-4, -5, -6, and -7), 120.58 (1, pyridine C-2), 134.01, 145.90 (0, Bt C-3a and -7a), 149.66 (1, pyridine C-2), and 150.34 (0, pyridine C-4); *m/z* 281 (M^+, 3%), 163 (32), 132 (100), 118 (21), 104 (31), 91 (10), 78 (13), and 77 (90) [Found (HRMS): *M*, 281.12682. $C_{15}H_{15}N_5O$ requires *M*, 281.12766].

2-(*Benzotriazol*-1-*ylmethyl*)*isoxazolidine*-5-*carbonitrile* (**9**).—The hydroxylamine (**1**) (2.0 g, 6.9 × 10^{-3} mol) was suspended in toluene (18 ml). Acrylonitrile (0.36 g, 6.9 × 10^{-3} mol) was added and the mixture heated under reflux for 15 h. The solvent was removed under reduced pressure and the crude product dissolved in $CHCl_3$. A precipitate formed with time, and this was filtered off and recrystallised from $CHCl_3$; yield 1.36 g, (88%), m.p. 109–110 °C; δ_H 2.30 (1 H, m, 4-H), 2.50 (1 H, m, 4-H′), 2.95 (1 H, t, 8.5 Hz, 3-H), 3.40 (1 H, m, 3-H′), 4.59 (1 H, dd, 8.8 Hz, 3.7 Hz, 5-H), 5.78 (1 H, d, 14.4 Hz, NC*H*H′N), 5.87 (1 H, d, 14.4 Hz, NCH*H*′N), 7.40 (1 H, t, 8.3 Hz) and 7.54 (1 H, t, 8.3 Hz, Bt 5-H and 6-H), and 7.71 and 8.06 (1 H, d, 8.3 Hz, Bt 4-H and 7-H); δ_C 34.55 (2, C-4), 48.47 (2, C-3), 64.57 (2, NCH_2N), 65.29 (1, C-5), 110.55, 119.69, 124.30, 128.07 (1, Bt C-4, -5, -6, and -7), 118.11 (0, CN), 133.91, and 145.82 (0, Bt C-3a and -7a); *m/z* 230 (M^+ + 1, 2%), 203 (2), 158 (4), 133 (9), 132 (89), 111 (100), 104 (28), 77 (90), and 51 (26); ν_{max}(Nujol) 1 613 (w, CN) (Found: C, 57.65; H, 4.8; N, 30.55. $C_{11}H_{11}N_5O$ requires C, 57.26; H, 4.76; N, 30.81%).

Dimethyl trans-2-(*Benzotriazol*-1-*ylmethyl*)*isoxazolidine*-4,5-*dicarboxylate* (**10**).—The hydroxylamine (**1**) (2.0 g, 6.9 × 10^{-3} mol) was suspended in toluene (18 ml). *trans*-Dimethylbutenedioate (0.99 g, 6.9 × 10^{-3} mol) was added and the mixture heated under reflux for 12 h. The solvent was removed under reduced pressure and the crude product separated into its components by flash chromatography using $CHCl_3$–THF (30:1) as eluant; yield 2.00 g (91%), m.p. 95–97 °C; δ_H 3.13 (1 H, t, 8.7 Hz, 3-H), 3.45 (1 H, t, 8.7 Hz, 3-H′), 3.66 (3 H, s, 4-Me), 3.67 (3 H, s, 5-Me), 3.72 (1 H, m, 4-H), 4.81 (1 H, d, 4.8 Hz, 5-H), 5.75 (1 H, d, 14.6 Hz, NC*H*H′N), 5.84 (1 H, d, 14.6 Hz, NCH*H*′N), 7.38 (1 H, t, 7.2 Hz) and 7.51 (1 H, t, 7.0 Hz, Bt 5-H and 6-H), and

7.57 (1 H, d, 8.3 Hz) and 8.05 (1 H, d, 8.3 Hz, Bt 4-H and 7-H); δ_C 50.30 (1, C-4), 52.15 (2, C-3), 52.29 (3, 4-Me), 52.40 (3, 5-Me), 65.05 (2, NCH_2N), 77.00 (1, C-5), 110.73, 119.21, 123.80, 127.43 (1, Bt C-4, -5, -6, and -7), 133.72, 145.58 (0, Bt C-3a and -7a), 170.04 (0, 4-CO), and 170.18 (0, 5-CO); *m/z* 320 (M^+, 2%), 261 (3), 203 (8), 202 (78), 133 (12), 132 (100), 104 (52), 78 (15), and 77 (99); ν_{max}(Nujol) 1 731 and 1 760 (s, CO) (Found: C, 52.45; H, 5.0; N, 17.7. $C_{14}H_{16}N_4O_5$ requires C, 52.50; H, 5.00; N, 17.50%).

Reaction of the Hydroxylamine (**1**) *with Cyclohex-2-enone.*—The hydroxylamine (**1**) (0.2 g, 6.8×10^{-4} mol) was dissolved in toluene (5 ml). Cyclohex-2-enone (0.13 g, 1.35×10^{-3} mol) was added and the mixture heated under reflux for 16 h. The solvent was removed under reduced pressure. Several components were evident on TLC analysis ($CHCl_3$); however, it was evident from ^1H NMR analysis that no isoxazolidine was present. 3-Benzotriazol-1-ylcyclohexanone (oil) (**13**) was isolated by flash chromatography using $CHCl_3$ as eluant; yield 0.1 g (68%); δ_H 1.76–1.92 (1 H, m), 2.14–2.26 (1 H, m), 2.32–2.62 (4 H, m), 2.98 (1 H, dd, 14.7 Hz, 5.7 Hz), 3.31 (1 H, dd, 14.7 Hz, 11.5 Hz), 5.08 (1 H, m, all cyclohexane-H), 7.36–7.61 (3 H, m), and 8.11 (1 H, d, 7.6 Hz, Bt 4-, 5-, 6-, and 7-H); δ_C 21.89, 31.00, 40.56, 47.07 (2, CH_2), 56.85 (1, *C*HCH_2), 109.05, 120.23, 124.19, 127.48 (1, Bt C-4, -5, -6, and -7), 132.09 and 146.04 (0, C-3a and -7a), 206.79 (0, CO).

Reaction of 2-(*Benzotriazol-1-ylmethyl*)-5-(2-*pyridyl*)*isoxazolidine* (**7**) *with* $NaBH_4$.—The isoxazolidine (**7**) (0.11 g, 3.77×10^{-4} mol) was dissolved in absolute ethanol (10 ml). $NaBH_4$ was added (0.018 g, 4.71×10^{-4} mol) and the solution heated under reflux under N_2 for 20 h. The mixture was poured into water (100 ml) and extracted with CH_2Cl_2. The extract was dried ($MgSO_4$), filtered, and the solvent removed under reduced pressure. The product was purified by flash chromatography using Et_2O as eluant. 2-Methyl-5-(2-pyridyl)isoxazolidine (**14**) (0.037 g, 60%), oil; δ_H (all lines are poorly resolved due to slow isoxazolidine nitrogen inversion) 2.47 (1 H, m, 4-H), 2.61–2.98 (2 H, m, 4-H′ and 3-H), 2.81 (3 H, br s, Me), 3.37 (1 H, m, 3-H′), 5.10–5.35 (1 H, m, 5-H), 7.17 (1 H, m, pyridine 5-H), 7.55 (1 H, m, pyridine 3-H), 7.68 (1 H, t, 6.3 Hz, pyridine 4-H), and 8.55 (1 H, br s, pyridine 6-H); δ_C (most of the resonances appear as uneven doublets due to observation of both stereoisomers produced by slow isoxazolidine nitrogen inversion: the smaller resonance signal is given in parentheses) 36.00 (3, Me), 45.40 [45.61] (2, C-4), 56.89 [57.15] (2, C-3), 78.76 [80.48] (1, C-5), 119.93 [120.93], 122.13 [122.47], 136.72 [136.62], and 148.99 [148.86] (1, pyridine C-3, -4, -5, and -6), and 162.47 (0, pyridine C-2); *m/z* 165 (M + 1, 100%), 164 (M^+, 6%), 134 (8), 122 (12), 118 (14), 108 (18), 106 (32), 105 (11), 79 (8), and 58 (15) [Found (HRMS): M, 164.095 75. $C_9H_{12}N_2O$ requires M, 164.094 96]. A small sample of the isoxazolidine (**14**) (*ca.* 0.02 g) was dissolved in ethanol (5 ml) and a large excess of saturated ethanolic picric acid (*ca.* 2 ml) was added. The green precipitate was filtered off at the pump, and recrystallised from aqueous ethanol. 2-Methyl-5-pyridin-2-ioisoxazolidinium dipicrate, m.p. dec. > 135 °C (Found: C, 40.2; H, 2.85; N, 17.75. $C_{21}H_{18}N_0O_{15}$ requires C, 40.52; H, 2.91; N, 18.00%).

Reaction of 2-(*Benzotriazol-1-ylmethyl*)-5-(4-*pyridyl*)*isoxazolidine* (**8**) *with* $NaBH_4$.—The isoxazolidine (**8**) (0.19 g, 6.78×10^{-4} mol) was dissolved in absolute ethanol (10 ml). $NaBH_4$ (0.05 g, 1.36×10^{-3} mol) was added and the mixture refluxed for 18 h. The solution was poured into water and extracted with $CHCl_3$. The extract was dried ($MgSO_4$), filtered, and the solvent removed under reduced pressure. The product was purified with a Chromatatron using 1:1, $CHCl_3$–EtOAc as eluant to give 2-methyl-5-(4-pyridyl)isoxazolidine (**15**) (0.075 g, 68%); δ_H (all lines are poorly resolved due to slow isoxazolidine nitrogen inversion) 2.20 (1 H, br s, 4-H), 2.55 (1 H, br s, 4′-H), 2.60–2.80 (1 H, br m, 3-H), 2.80 (3 H, br s, Me), 3.37 (1 H, br s, 3-H′), 5.96–6.12 (1 H, br m, 5-H), 7.29 (2 H, d, 4.9 Hz, pyridine 3-H), and 8.55 (2 H, d, 4.9 Hz, pyridine 2-H); δ_C (most of the resonances appear as broadened lines consisting essentially of doublets, due to observation of both stereoisomers produced by slow isoxazolidine nitrogen inversion: the centre of resonance is recorded) 37.29 (2, C-4), 45.43 (3, Me), 56.79 (2, C-3), 76.42 (1, C-5), 120.79 (1, pyridine C-3), and 149.72 (1, pyridine C-2); the resonance of C-4 was not observed; *m/z* 164 (63%), 132 (12), 119 (100), 118 (96), 106 (19), 105 (62), 104 (27), 91 (19), 79 (16), 78 (38), 59 (17), 52 (24), and 51 (42) [Found (HRMS): M, 164.09444. $C_9H_{12}N_2O$ requires M, 164.09496].

A small sample of the isoxazolidine (**15**) (*ca.* 0.02 g) was dissolved in ethanol (5 ml). A large excess of ethanolic saturated picric acid (*ca.* 2 ml) was added and the yellow precipitate collected at the pump. The product was recrystallised from aqueous ethanol to give 2-methyl-5-(pyridinio)isoxazolidinium dipicrate, m.p. decomp. < 142 °C (Found: C, 40.3; H, 2.8; N, 17.7. $C_{21}H_{18}N_8O_{15}$ requires C, 40.52; H, 2.91; N, 18.00%).

Reaction of 2-(*Benzotriazol-1-ylmethyl*)-5-(2-*pyridyl*)*isoxazolidine* (**7**) *with Perchloric Acid.*—The isoxazolidine (**7**) (0.95 g, 3.37×10^{-3} mol) was dissolved in ethanol (20 ml). Aqueous 70% perchloric acid (0.58 ml, 6.74×10^{-3} mol) was added and the mixture refluxed for 15 min. On cooling, the precipitate was filtered off at the pump and recrystallised from ethanol to give 12-oxa-1,3-diazatricyclo[7.2.1.$0^{3,8}$]dodec-3,5,7-triene-3-ium perchlorate (**17**) (0.60 g, 64%), m.p. 121–122 °C; δ_H[$(CD_3)_2SO$] 2.61 (2 H, m, 10-H), 3.50 (2 H, m, 11-H), 5.53 (1 H, d, 14.0 Hz, 2-H), 5.81 (1 H, d, 3.4 Hz, 9-H), 5.98 (1 H, d, 14.0 Hz, 2-H′), 7.99 (1 H, d, 8.0 Hz, 7-H, 8.07 (1 H, dd, 6.2 Hz, 7.6 Hz, 5-H), 8.57 (1 H, d, 7.6 Hz, 6-H), and 8.75 (1 H, d, 6.2 Hz, 4-H); δ_C[$(CD_3)_2SO$] 39.27 (2, C-10), 50.92 (2, C-11), 71.07 (1, C-9), 76.24 (2, C-2), 124.57 and 126.64 (1, C-5 and -7), 143.16 (1, C-6), 146.08 (1, C-4), and 153.04 (0, C-8) (Found: C, 41.15; H, 4.2; N, 10.35. $C_9H_{11}ClN_2O_5$ requires C, 41.00; H, 4.59; N, 10.62%). On further refluxing of (**7**) (0.43 g, 1.5×10^{-3} mol) in the ethanolic perchloric acid solution (> 30 min) no precipitate formed on cooling. The mixture was poured into aqueous saturated Na_2CO_3 (50 ml) and extracted with $CHCl_3$. The extract was dried ($MgSO_4$), filtered, and the solvent removed under reduced pressure. The product was purified by flash chromatography using $CHCl_3$ as eluant to give bis[5-(2-pyridyl)isoxazolidin-2-yl]methane (**19**), (0.21 g, 85%); δ_H 2.45 (2 H, m, 4-H), 2.84 (2 H, m, 4-H′), 3.25 (4 H, m, 3-H), 4.06 (2 H, s, NCH_2N), 5.30 (2 H, dd, 8.7 Hz, 5.7 Hz, 5-H), 7.17 (2 H, m) and 7.58–7.70 (4 H, m, pyridine 3-, 4-, and 5-H), and 8.54 (2 H, d, 4.2 Hz, pyridine 6-H); δ_C (several resonances appear as doublets due to observation of rotamers) 35.48 and 35.54 (2, C-4), 52.69 and 52.75 (2, C-3), 79.12 (2, NCH_2N), 79.86 (1, C-5), 120.56 and 122.23 (1, pyridine C-3 and C-5), 136.51 and 136.53 (1, pyridine C-2), 148.88 (1, pyridine C-2), and 161.30 and 161.39 (0, pyridine C-2); *m/z* (chemical impact) 312 (M^+, 4%), 311 (23), 281 (23), 204 (33), 178 (16), 120 (40), and 118 (100).

Reaction of 2-(*Benzotriazol-1-yl*)-5-(4-*pyridyl*)*isoxazolidine* (**8**) *with Perchloric Acid.*—The isoxazolidine (**8**) (0.23 g, 8.26×10^{-4} mol) was dissolved in ethanol (10 ml). Perchloric acid (70% aqueous; 0.16 ml, 1.16×10^{-3} mol) was added and the mixture refluxed for 30 min. The solution was poured into aqueous saturated Na_2CO_3 and extracted with $CHCl_3$. The extract was dried ($MgSO_4$), filtered, and the solvent removed under reduced pressure. The product was purified by flash chromatography using Et_2O as eluant to give 5-(4-pyridyl)-isoxazolidine (**16**) as an oil (0.057 g, 46%); δ_H 2.15 (1 H, sextet,

6.5 Hz, 4-H), 2.72 (1 H, m, 4-H'), 3.30 (2 H, m, 3-H), 4.99 (1 H, br t, 7.0 Hz, 5-H), 7.28 (2 H, d, 6.0 Hz, pyridine 3-H), and 8.58 (2 H, d, 6.0 Hz, pyridine 2-H); δ_C 38.48 (2, C-4), 49.08 (2, C-3), 80.46 (1, C-5), 120.78 (1, pyridine C-3), 150.00 (1, pyridine C-2), and 149.79 (0, pyridine (C-4); ν_{max} 3 389 (s, NH); *m/z* 151 (M^+, 11%), 150 (40), 133 (12), 119 (59), 118 (100), 117 (31), 106 (40), 105 (62), 104 (36), 91 (29), 78 (47), and 51 (67) [Found (HRMS): *M*, 150.07897. $C_8H_{10}N_2O$ requires *M*, 150.07931].

Reduction of 12-Oxa-1,3-diazatricyclo[7.2.1.0^{3,8}]*dodeca-3,5,7-trien-3-ium Perchlorate* (**17**) *with* $NaBH_4$.—The perchlorate (**17**) (1.0 g, 3.8 × 10^{-3} mol) was dissolved in ethanol (15 ml). $NaBH_4$ (0.36 g, 9.5 × 10^{-3} mol) was added and the mixture refluxed for 1.5 h. The solution was poured into water (50 ml) and extracted with $CHCl_3$. The product was purified by flash chromatography using EtOAc as eluant and recrystallised from pentane to give 12-oxa-1,3-diazatricyclo[7.2.1.0^{3,8}]dodec-5-ene [**18**), m.p. 78–79 °C, 0.5 g (81%); δ_H 1.87 (2 H, m, 7-H), 2.06 (1 H, m, 10-H), 2.41 (1 H, m, 10-H'), 2.66 (2 H, m, 4-and 8-H), 3.00 (1 H, d, 15.0 Hz, 4-H'), 3.23 (2 H, m, 11-H), 3.60 (1 H, d, 11.0 Hz, 2-H), 3.68 (1-H, d, 11.0 Hz, 2-H'), 4.14 (1 H, d, 6.9 Hz, 9-H), and 5.70 (2 H, m, 5- and 6-H); δ_C 27.18 (2, C-7), 29.72 (2, C-10), 48.56 (2, C-4), 52.18 (2, C-11), 58.92 (1, C-8), 77.38 (2, C-2), 77.47 (1, C-9), 123.89 (1, C-6), and 124.36 (1, C-5); *m/z* 167 (M^+ + 1, 32%), 166 (M^+ 3%), 165 (5), 123 (84), 94 (15), 82 (100), 80 (50), 67 (14), 55 (19), 54 (33), and 42 (78) (Found: C, 64.9; H, 8.65; N, 16.7. $C_9H_{14}N_2O$ requires C, 65.03; H, 8.49; N, 16.85%).

Reaction of Benzotriazol-1-ylmethylene(benzotriazol-1-ylmethyl)amine (**3**) *with Methyl Acrylate*.—The amine (**3**) (0.05 g, 1.8 × 10^{-4} mol) was dissolved in dry toluene (5 ml). Methyl acrylate (0.05 g, 5.4 × 10^{-4} mol) was added together with trifluoroacetic acid (0.1 g, 1.3 × 10^{-3} mol). The mixture was heated under reflux for 24 h and the solvent was removed under reduced pressure. The major product was purified by flash chromatography using $CHCl_3$ as eluant, to give a mixture of methyl 3-benzotriazol-1-yl- and methyl 3-benzotriazol-2-yl-propanoate (**11**) (0.070 g; 95% of available benzotriazolate). The two isomers may be separated by repeated chromatography. Methyl 3-benzotriazol-1-ylpropanoate (oil); δ_H 3.12 (2 H, t, 7.4 Hz, 2-H), 4.91 (2 H, t, 7.4 Hz, 3-H), 7.34 (1 H, m, 7.52 (1 H, m, Bt 5-H and 6-H), 7.64 (1 H d, 8.3 Hz) and 8.06 (1 H, d, 8.3 Hz, Bt 4-H and 7-H); δ_C 34.10 (2, C-2), 43.33 (2, C-3), 52.13 (3, Me), 109.52, 119.91, 123.97, 127.46 (1, Bt C-4, -5, -6, and -7), 133.07, 145.84 (0, C-3a and -7a). Methyl 3-benzotriazol-2-ylpropanoate (oil); δ_H 3.19 (2 H, t, 7.4 Hz, 2-H), 3.74 (3 H, s, Me), 5.05 (2 H, t, 7.4 Hz, 3-H), 7.39 (2 H, m, Bt 5-H and 6-H), and 7.88 (2 H, m, Bt 4-H and 7-H); 33.89 (2, C-2), 51.66 (2, C-3), 52.14 (3, Me), 118.03, 126.41 (1, Bt C-4 and -5), 144 (0, Bt C-3a), and 170.67 (0, CO).

Reaction of Benzotriazol-1-ylmethylene(benzotriazol-1-ylmethyl)amine (**3**) *with* N-*Methylmaleimide*.—The amine (**3**) (0.05 g, 1.8 × 10^{-4} mol) was suspended in toluene (3 ml). *N*-Methylmaleimide (0.06 g, 5.4 × 10^{-4} mol) was added, together with trifluoroacetic acid (0.05 ml, 7.0 × 10^{-4} mol). The mixture was heated under reflux under N_2 for 48 h. The solvent was removed under reduced pressure. The major product was purified by flash chromatography using $CHCl_3$ as eluant to give *N*-methyl-3-benzotriazol-1-ylsuccinimide (**12**) (0.041 g; 99% of available benzotriazolate). Recrystallised from toluene–hexane, m.p. 127–128 °C; δ_H 3.14 (3 H, s, Me), 3.48 (1 H, dd, 18.3 Hz, 9.5 Hz, C*H*H'), 3.65 (1 H, dd, 18.3 Hz, 5.4 Hz, CH*H'*), 5.84 (1 H, dd, 9.5 Hz, 5.4 Hz, CH_2CH), 7.43 (1 H, m), 7.55 (2 H, m), and 8.1 (1 H, d, 9.3 Hz, Bt 4-, 5-, 6-, and 7-H); δ_C 25.54 (3, Me), 34.85 (2, CH_2), 55.54 (1, CH), 108.98, 120.50, 124.70, 128.48 (1, Bt C-4, -5, -6, and -7), 133.09, 146.13 (0, Bt C-4a and -7a), 171.79, and 173.05 (0, CO); *m/z* 230 (M^+, 32%), 201 (30), 174 (21), 173 (50), 148 (18), 117 (31), 103 (100), 91 (34), 90 (22), 76 (45), and 55 (100); ν_{max}(Nujol) 1 800 and 1 730 (s, CO) (Found: C, 57.05; H, 4.3; N, 24.45. C requires C, 57.39; H, 4.38; N, 24.34%).

Reaction of Benzotriazol-1-ylmethylene(benzotriazol-1-ylmethyl)amine (**3**) *with Dimethyl Butynedioate*.—The amine (**3**) (0.05 g, 1.8 × 10^{-4} mol) was suspended in toluene (5 ml). Dimethyl butynedioate (0.08 g, 5.4 × 10^{-4} mol) was added together with trifluoroacetic acid (0.05 ml, 7.0 × 10^{-4} mol). The mixture was heated under reflux under N_2 for 16 h. The solvent was removed under reduced pressure and a single pair of diastereoisomeric products were purified by flash chromatography using $CHCl_3$ as eluant. Mixture of *cis*- and *trans*-dimethyl 2-benzotriazol-1-ylbutenedioate (**20**) (oil) (77 mg, 2.9 × 10^{-4} mol, 82%). Further chromatography ($CHCl_3$) resulted in the isolation of pure samples of each isomeric alkene, although stereochemical identification has not been made. In order of elution; 1. Diastereoisomer of higher R_f ($CHCl_3$), recrystallised from hexane–toluene, m.p. 72–74 °C; δ_H 3.88 (3 H, s, Me), 4.07 (3 H, s, Me), 6.69 (1 H, s, =CH), 7.46–7.54 (1 H, m), 7.62–7.66 (2 H, m), and 8.18 (1 H, d, 8.5 Hz, Bt 4-, 5-, 6-, and 7-H); *m/z* 262 (*M* + 1, 70%), 261 (M^+, 70), 202 (38), 175 (58), 174 (40), 173 (46), 159 (51), 146 (23), 132 (29), 115 (42), 103 (28), 92 (38), 89 (38), 77 (68), and 76 (56) [Found (HRMS): *M*, 261.0749. $C_{12}H_{11}N_3O_4$ requires *M*, 261.0752]; ν_{max}(Nujol) 1 742 and 1 713 (s, CO). 2. Diastereoisomer of lower R_f ($CHCl_3$), recrystallised from toluene–hexane, m.p. 59–60 °C; δ_H 3.57 (3 H, s, Me), 3.89 (3 H, s, Me), 7.27 [1 H, s, =C*H*(CO_2Me)], 7.35–7.58 (3 H, m), and 8.13 (1 H, d, 8.8 Hz, Bt 4-, 5-, 6-, and 7-H); δ_C 52.54 (3, Me), 53.72 (3, Me), 110.04, 120.29, 124.34, 128.52 (1, Bt C-4, -5, -6, and -7), 128.57 (1, =CH), 133.50, 134.04, 145.50 [0, Bt C-3a, -7a, and =C(Bt)(CO_2Me)], 162.05, and 162.76 (0, CO); *m/z* 262 (*M* + 1, 23%), 261 (M^+, 77%), 202 (38), 175 (51), 174 (38), 173 (42), 160 (32), 159 (57), 132 (30), 115 (44), 105 (34), 103 (33), 92 (41), 89 (41), 77 (73), 76 (56), and 59 (100); ν_{max}(Nujol) 1 731 (br s, CO) (Found: C, 55.35; H, 4.25; N, 16.01. $C_{12}H_{11}N_3O_4$ requires C, 55.17; H, 4.24; N, 16.08%).

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