Synthesis and Transformations of 1-(1,3-Butadien-1-yl)benzotriazoles

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1-[α-(Phenylthio)alkyl]benzotriazoles were converted into the corresponding 1-(1,3-butadien-1-yl)benzotriazoles in good yields by one-pot sequential reactions with (i) lithium diisopropylamide, (ii) allyl bromide or cinnamyl chloride, and (iii) potassium *t*-butoxide. Diels-Alder and hetero [4+2] cycloadditions of 1-(1,3-butadien-1-yl)benzotriazoles and some transformations of their α-lithio derivatives were studied.

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The preparation of novel functionalized benzotriazoles and the exploration of their synthetic potential has recently received much attention in our group [1]. In continuation of these studies, we now report the preparation and some reactions of representative 1-(1,3-butadien-1-yl)benzotriazoles.

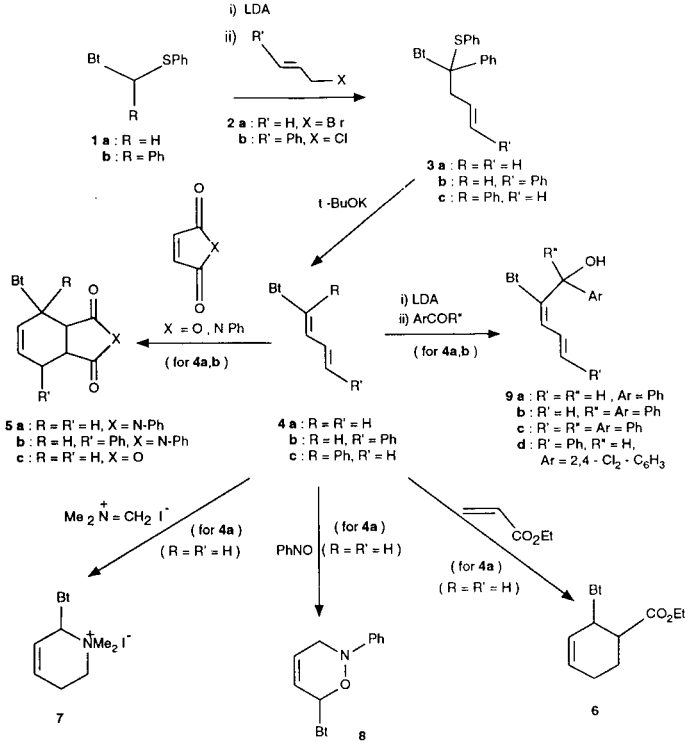
Results and Discussion.

α-Lithio derivatives of 1-[α-(phenylthio)alkyl]benzotriazoles **1a,b** generated *in situ* from compounds **1** and lithium diisopropylamide in THF at -78° (*cf.* ref [2]) reacted readily with allyl bromide **2a** or cinnamyl chloride **2b** to afford the corresponding allylated intermediates **3a-c**, which were identified spectroscopically, but converted directly into 1-(1,3-butadien-1-yl)benzotriazoles **4a-c** by potassium *t*-butoxide at 25° (Scheme 1). Optimal reaction conditions, including the use of two equivalents of potassium *t*-butoxide, enabled the synthesis of compounds **4a-c** in 60-75% yield.

Compound **4b** has been previously prepared in 56% yield by the Wittig reaction of (benzotriazol-1-yl)methylenetriphenylphosphorane with cinnamaldehyde [3]. The availability of a variety of stable *N*-[α-(substituted-thio)alkyl]benzotriazoles from benzotriazole, thiols and aldehydes or ketones [3] makes the present route preferable to the earlier method *via* phosphoranes which is restricted by the instability of the *N*-(α-chloroalkyl)benzotriazole precursors (except for the simplest 1-chloromethylbenzotriazole), and by the fact that *N*-(α-chloro-α-arylmethyl)benzotriazoles are still unknown [4].

The structures of new compounds **4a,c** were confirmed by their spectral and analytical data. In the ^{1}H nmr spectra of 1-(1,3-butadien-1-yl)benzotriazoles **4a,c**, the terminal methylene group appeared as an AB system coupled with the protons in position 2 of the butadienyl fragment. 1-(1,3-Butadien-1-yl)benzotriazole **4a** was isolated as the pure *trans*-isomer, as evidenced by the observed value of *ca.* 10 Hz of the coupling constant between the protons in the positions 1 and 2. A COSY nmr experiment confirmed the assignment to H-1 of the signal at δ 7.20 ppm, which resonates close to the benzotriazole protons. The analogous *E*-structure is assigned tentatively to compound **4c** ($J_{2,3}$ = 13.2 Hz).

Scheme 1



1,3-Butadienes are of generally recognized value in synthetic organic chemistry due to their key role in Diels-Alder reactions, including hetero [4+2] transformations leading to various types of heterocycles (for a review see [5]). Indeed, compounds **4a,b** readily formed the corresponding cycloadducts **5a-c** and **6** upon heating at 110° in toluene with *N*-phenylmaleimide, maleic anhydride and ethyl acrylate, respectively (Scheme 1). We obtained the substituted cyclohexene **6** as a mixture of two diastereomers in a ratio of *ca.* 1:1.2 (by ^{1}H and ^{13}C nmr spectra; it was reported [6] that the analogous reaction of 1-phenyl-1,3-butadiene resulted in a mixture of the "*ortho*" and "*meta*" isomers in a ratio of 39:1). The structure of this product was confirmed by nmr decoupling experiments,

which revealed the vicinal relationship of HC(Bt) and HC(CO_2Et) protons at *ca.* 5.7 and 3.4-3.5 ppm, respectively. Compounds **5** and **6** appeared to be remarkably stable as compared to analogous cycloadducts of dieneamines [7] and did not eliminate benzotriazole under a variety of thermal and acidic conditions, thus reflecting a relatively low leaving ability of the neutral or protonated benzotriazole which may be attributed to its π-deficient character (*cf.* ref [1]).

Hetero Diels-Alder reaction of 1-(1,3-butadien-1-yl)benzotriazole **4a** with Eschenmoser's salt in methylene chloride at 25° afforded the expected 1,2,5,6-tetrahydropyridinium salt **7** in 77% yield (Scheme 1). The structure of this compound was confirmed by its spectral data: the ^{13}C nmr APT spectrum of **7** in DMSO-d_6 displayed two signals for the methylene groups at δ 20.9 (C-5) and 57.8 ppm (C-6), thus excluding the alternative structure with the (benzotriazol-1-yl) substituent in the 3-position. To our knowledge, the only other hetero [4+2] cycloaddition of Eschenmoser's salt is with 1-methoxy-3-trimethylsilyloxy-1,3-butadiene, as reported by Danishefsky *et al.* [8] (*cf.* also ref [9]).

1-(1,3-Butadien-1-yl)benzotriazole **4a** readily reacted with nitrosobenzene under mild conditions to give the substituted dihydro-1,2-oxazine **8** in high yield (Scheme 1). The structure of product **8** was established by X-ray analysis. Figure 1 shows the crystal structure and the atom labeling of the oxazine **8** (in perspective). Tables 1 and 2 list the atom coordinates and bond geometries. The X-ray determination shows the structure to be that of 6-(benzotriazol-1-yl)-2-phenyl-3,6-dihydro-1,2-oxazine. The oxazine ring exists in a half chair conformation with the phenyl ring equatorial and the benzotriazolyl group axial. The benzotriazole ring system is planar to within 0.005 Å and is orthogonal to the plane of the oxazine ring (angle between meanplanes = 91.9(2)°). The phenyl ring is planar to within 0.006 Å and is inclined to the oxazine meanplane at an angle of 17.9(2)°. The bonding geometry shows no unusual features and there are no intermolecular contacts less than 3.2 Å.

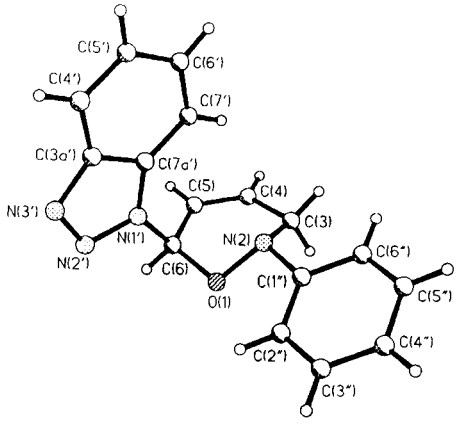


Figure 1. X-Ray structure and atom labeling of the oxazine.

Table 1

Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Coefficients (Å^{2}x10^3) for the Oxazine

Atom	x	y	z	U_{eq} [a]
O(1)	1138(2)	187(2)	6347(1)	26(1)
N(2)	1629(3)	1463(2)	6746(1)	24(1)
C(3)	3748(3)	1533(3)	6826(1)	33(1)
C(4)	4570(4)	1706(3)	6289(1)	32(1)
C(5)	3502(3)	1463(3)	5830(1)	29(1)
C(6)	1490(3)	824(3)	5832(1)	25(1)
N(1')	11(3)	2009(2)	5637(1)	23(1)
N(2')	-1548(3)	1435(3)	5314(1)	27(1)
N(3')	-2690(3)	2654(3)	5178(1)	28(1)
C(3A')	-1898(3)	4072(3)	5414(1)	24(1)
C(4')	-2577(3)	5692(3)	5385(1)	29(1)
C(5')	-1468(4)	6866(3)	5660(1)	31(1)
C(6')	276(4)	6442(3)	5963(1)	29(1)
C(7')	955(3)	4857(3)	5998(1)	28(1)
C(7A')	-166(3)	3674(3)	5712(1)	22(1)
C(1")	633(3)	1110(3)	7210(1)	23(1)
C(2")	-965(3)	63(3)	7183(1)	27(1)
C(3")	-1970(3)	-180(3)	7638(1)	34(1)
C(4")	-1431(4)	623(3)	8118(1)	35(1)
C(5")	153(4)	1661(3)	8145(1)	35(1)
C(6")	1193(4)	1894(3)	7700(1)	31(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2

Bond Lengths (Å) Angles (°)

O(1)-N(2)	1.458(2)	O(1)-C(6)	1.423(3)
N(2)-C(3)	1.470(3)	N(2)-C(1")	1.424(3)
C(3)-C(4)	1.502(4)	C(4)-C(5)	1.324(4)
C(5)-C(6)	1.492(3)	C(6)-N(1')	1.463(3)
N(1')-N(2')	1.374(3)	N(1')-C(7A')	1.377(3)
N(2')-C(3')	1.299(3)	N(3')-C(3A')	1.390(3)
C(3A')-C(4')	1.402(3)	C(3A')-C(77A')	1.397(3)
C(4')-C(5')	1.374(3)	C(5')-C(6')	1.415(3)
C(6')-C(7')	1.376(3)	C(7')-C(7A')	1.397(3)
C(1")-C(2")	1.397(3)	C(1")-C(6")	1.405(3)
C(2")-C(3")	1.391(4)	C(3")-(4")	1.386(4)
C(4")-C(5")	1.385(4)	C(5")-C(6")	1.385(4)
N(2)-O(1)-C(6)	107.7(2)	O(1)-N(2)-C(3)	107.1(2)
O(1)-N(2)-C(1")	107.8(2)	C(3)-N(2)-C(1")	116.6(2)
N(2)-C(3)-C(4)	109.5(2)	C(3)-C(4)-C(5)	121.7(2)
C(4)-C(5)-C(6)	120.4(2)	O(1)-C(6)-C(5)	111.3(2)
O(1)-C(6)-N(1')	111.8(2)	C(5)-C(6)-N(1')	113.6(2)
C(6)-N(1')-N(2')	117.8(2)	C(6)-N(1')-C(7A')	132.4(2)
N(2')-N(1')-C(7A')	109.9(2)	N(1')-N(2')-N(3')	109.0(2)
N(2')-N(3')-C(3A')	108.3(2)	N(3')-C(3A')-C(4')	130.0(2)
N(3')-C(3A')-C(7A')	108.9(2)	C(4')-C(3A')-C(7A')	121.2(2)
C(3A')-C(4')-C(5')	117.3(2)	C(4')-C(5')-C(6')	121.0(2)
C(5')-C(6')-C(7')	122.4(2)	C(6')-C(7')-C(7A')	116.3(2)
N(1')-C(7A')-C(3A')	103.9(2)	N(1')-C(7A')-C(7')	134.2(2)
C(3A')-C(7A')-C(7')	121.9(2)	N(2)-C(1")-C(2")	121.6(2)
N(2)-C(1")-C(6")	119.6(2)	C(2")-C(1")-C(6")	118.7(2)
C(1")-C(2")-C(3')	120.0(2)	C(2")-C(3")-C(4")	121.0(2)
C(3")-C(4")-C(5")	119.2(2)	C(4")-C(5")-C(6')	120.6(2)
C(1")-C(6")-C(5")	120.5(2)		

Compounds **7** and **8** bearing the benzotriazolyl group in a position α to nitrogen or oxygen atoms, respectively, possess potential for further synthetic transformations involving nucleophilic displacement of benzotriazole (*cf.* review [1]).

Previous work in our group has demonstrated the ability of a *N*-benzotriazolyl substituent to assist the formation of α-carbanions [1,10]. We now report on some analogous transformations of the 1-(1,3-butadien-1-yl)benzotriazoles **4a,b**. Compounds **4a,b** underwent regioselective α-lithiation under the action of lithium diisopropylamide in tetrahydrofuran. The resulting lithio derivatives were trapped with benzaldehyde or aromatic ketones to afford compounds **9** in high yield (Scheme 1). The *E*-configuration of the substituents in positions 2,3 of the dienes **9** was established by nmr NOE experiments. Thus, in the nmr spectra of compound **9a**, irradiation of the 1-H singlet at δ 6.31 ppm resulted in an 8% nuclear Overhauser enhancement of the 4-H resonance (δ 7.07 ppm) and did not affect the other olefinic resonances. Irradiation of the 3-H signal at δ 6.61 (J_{trans} = 11.1 Hz) by contrast affected only the 7-H Bt resonances (δ 7.44 ppm, 10% enhancement) and that of the 5-H proton (δ 5.60 ppm, 7% enhancement). In agreement with this assignment, irradiation of the 5-H signals resulted in 10% and 8% enhancements for the resonances of the 4-H and 3-H protons, respectively. These data clearly indicate the *s-trans*-configuration for molecules **9**. The *E*-configuration of the substituents in positions 4 and 5 of diene **9d** was assigned based on the *trans* coupling constant of *ca.* 11.3 Hz between the 4-H and 5-H protons. Lithiations of dieneamines have apparently not previously been reported (*cf.* ref [7]). Further studies of the reactivity of the new substituted benzotriazoles **7-9** are currently underway in our group.

In conclusion, we have described a three-step one-pot transformation of 1-[α-(phenylthio)alkyl]benzotriazoles **1** which provides a new and simple route to 1-(1,3-butadien-1-yl)benzotriazoles **4**. These products combine two useful organic functionalities in a single molecular framework and are capable of various synthetic transformations leading to novel benzotriazole derivatives.

EXPERIMENTAL

Melting points were recorded on a Thomas-Hoover melting point apparatus and are uncorrected. The ^{1}H (300 MHz) and ^{13}C (75 MHz) nmr spectra were obtained on Varian XL300 spectrometer. Microanalyses were performed at the University of Florida or Atlantic MicroLab Inc., Atlanta. Tetrahydrofuran (THF) and toluene were dried by distillation from sodium benzophenone ketyl. Column chromatography was carried out using E. M. Merck silica gel (230-400 mesh). All reactions with water sensitive compounds were carried out in a dry nitrogen atmosphere. Compounds **1a** and **1b** were prepared by the literature procedures of refs [11] and [2], respectively.

General Procedure for the Preparation of Butadienes **4a-c**.

Lithium diisopropylamide (LDA, 1.5 *M*) in cyclohexane (2.94 ml, 4.4 mmoles) was added dropwise to a solution of the appropriate compound, **1a,b**, (4 mmoles) in THF (20 ml) at -78°. After 15 minutes, allyl bromide (0.38 ml, 4.4 mmoles) or cinnamyl chloride (0.67 g, 4.4 mmoles) in THF (5 ml) was added dropwise at -78°. The mixture was stirred over 4 hours and allowed to warm up to 25°. Potassium *t*-butoxide (95%, 0.94 g, 8 mmoles) was added portionwise with stirring. The mixture was stirred over 12 hours and quenched with 10% aqueous ammonium chloride (20 ml) followed by extraction with diethyl ether (3 x 20 ml). Combined organic layers were washed with water (3 x 20 ml), 10% sodium hydroxide (4 x 20 ml), water (2 x 20 ml) and dried (magnesium sulfate). Evaporation of the solvent followed by column chromatography (eluent, hexane-diethyl ether) gave **3a-c** in 75, 60 and 60% yields, respectively.

1-(1,3-Butadien-1-yl)benzotriazole (**4a**).

This compound was obtained as colorless needles (hexane), mp 67-69°; ^{1}H nmr (deuteriochloroform): δ 8.09 (d, 1H, Bt, J = 8.1 Hz), 7.69 (d, 1H, Bt, J = 8.4 Hz), 7.56 (m, 1H, Bt), 7.50 (d, 1H, 1-H, J = 14.4 Hz), 7.42 (dd, 1H, Bt, J = 8.4, 8.1 Hz), 7.11 (m, 1H, 2-H), 6.54 (m, 1H, 3-H), 5.51 (d, 1H, CH_AH$_B$, J = 16.8 Hz), 5.30 (d, 1H, CH$_A$$H_B$, J = 10.2 Hz); ^{13}C nmr (deuteriochloroform): δ 146.0, 132.8, 131.1, 128.0, 124.4, 124.2, 121.2, 120.0, 119.9, 109.8.

Anal. Calcd. for $C_{10}H_9N_3$: C, 70.16; H, 5.26; N, 24.54. Found: C, 70.00; H, 5.30; N, 24.47.

1-[(1,3-Butadien-1-yl)-4-phenyl]benzotriazole (**4b**).

This compound was obtained as colorless needles (hexane), mp 148-150° (lit [2] mp 147-149°).

1-[(1,3-Butadien-1-yl)-1-phenyl]benzotriazole (**4c**).

This compound was obtained as an oil; ^{1}H nmr (deuteriochloroform): δ 8.02 (m, 1H, Bt), 7.50-7.10 (m, 8H, aromatic), 6.97 (d, 1H, 2-H, J = 13.2 Hz), 6.79-6.63 (m, 1H, 3-H), 5.60 (d, 1H, CH_AH$_B$, J = 16.2 Hz), 5.38 (d, 1H, CH$_A$$H_B$, J = 10.2 Hz); ^{13}C nmr (deuteriochloroform): δ 146.2, 135.7, 133.1, 132.6, 131.7, 129.5, 129.5, 128.7, 127.5, 125.8, 124.0, 122.3, 120.0, 111.2.

Anal. Calcd. for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.60; H, 5.29; N, 16.63.

General Procedure for the Preparation of Cycloadducts **5a-c** and **6**.

Butadienes **4a** or **4b** (0.6 mmole) and the appropriate dienophile (0.6 mmole) were heated at 110° in toluene for 3 hours (6 hours in case of **5**). The mixture was cooled to 25° and the products **5a-c** were filtered, washed with diethyl ether, ethanol and dried in vacuum. Compound **6** was isolated after the evaporation of the toluene, followed by column chromatography (eluent hexane-diethyl ether).

3-(Benzotriazol-1-yl)-1-phenyl-2,2a,3,6,6a,7-hexahydroisoindole-2,7-dione (**5a**).

This compound was obtained in 85% yield as a colorless needles (hexane), mp 232-233°; ^{1}H nmr (dimethyl sulphoxide-d$_6$): δ 8.05 (d, 1H, Bt, J = 8.4 Hz), 7.99 (d, 1H, Bt, J = 7.7 Hz), 7.58 (m, 1H, Bt), 7.45-7.28 (m, 4H, aromatic), 6.86 (dd, 2H, Ph, J = 6.9, 1.2 Hz), 6.45 (m, 1H, 4-H), 6.33 (m, 1H, 5-H), 6.19 (m, 1H, 3-H), 3.96 (dd, 1H, 2a-H, J = 9.0, 6.6 Hz), 3.70 (m, 1H, 6a-H), 2.91-2.48 (m, 2H, CH$_2$); ^{13}C nmr (dimethyl sulphoxide-d$_6$): δ 178.5 (C=O), 174.6 (C=O), 144.7, 133.2, 132.0, 132.0, 128.7, 128.2, 127.4,

126.5, 125.1, 124.1, 119.1, 110.7, 50.2 (C-3), 42.9 (C-2a), 37.2 (C-6a), 22.1 (C-6).

Anal. Calcd. for $C_{20}H_{16}N_4O_2$: C, 69.76; H, 4.65; N, 16.27. Found: C, 70.10; H, 4.67; N, 16.14.

3-(Benzotriazol-1-yl)-1,6-diphenyl-2,2a,3,6,6a,7-hexahydroisoindole-2,7-dione (**5b**).

This compound was obtained in 82% yield as colorless needles (hexane), mp 212-215°; ^{1}H nmr (dimethyl sulphoxide-d_6): δ 8.20-8.05 (m, 2H, Bt), 7.70-7.20 (m, 10H, aromatic), 7.05-6.90 (m, 3H, 2H Ph and 4-H), 6.74 (m, 1H, 5-H), 6.24 (m, 1H, 3-H), 4.20-4.10 (m, 2H, 2a-H and 6a-H), 3.93 (m, 1H, 6-H); ^{13}C nmr (dimethyl sulphoxide-d_6): δ 180.4 (C=O), 178.7 (C=O), 150.8, 144.8, 138.7, 137.5, 137.2, 134.1, 134.0, 133.5, 133.4, 132.6, 131.9, 131.7, 129.4, 124.7, 115.9, 59.0 (C-3), 50.8 (C-2a), 49.2 (C-6a), 45.1 (C-6).

Anal. Calcd. for $C_{26}H_{20}N_4O_2$: C, 74.27; H, 4.79; N, 13.32. Found: C, 74.50; H, 4.83; N, 13.15.

3-(Benzotriazol-1-yl)-2,2a,3,6,6a,7-hexahydroisobenzofuran-2,7-dione (**5c**).

This compound was obtained in 63% yield as a colorless solid, mp 209-211°; ^{1}H nmr (dimethyl sulphoxide-d_6): δ 8.08 (d, 1H, Bt, J = 8.1 Hz), 8.01 (d, 1H, Bt, J = 8.4 Hz), 7.62 (m, 1H, Bt), 7.45 (m, 1H, Bt), 6.51 (m, 1H, 4-H), 6.33 (m, 1H, 5-H), 6.16 (m, 1H, 3-H), 4.17 (m, 1H, 2a-H), 3.95 (m, 1H, 6a-H), 2.80-2.60 (m, 2H, CH_2); ^{13}C nmr (dimethyl sulphoxide-d_6): δ 174.6 (C=O), 170.4 (C=O), 144.9, 132.9, 131.5, 127.7, 125.3, 124.3, 119.3, 110.5, 50.3 (C-3), 43.7 (C-2a), 38.1 (C-6a), 22.2 (C-6).

Anal. Calcd. for $C_{14}H_{11}N_3O_3$: C, 62.45; H, 4.12; N, 15.61. Found: C, 61.76; H, 4.04; N, 15.37 (No better analysis could be obtained).

1-(Benzotriazol-1-yl)-6-ethoxycarbonylcyclohex-2-ene (**6**).

This compound was obtained as an oil (mixture of two diastereomers in a ratio of *ca.* 1:1.2); ^{1}H nmr (deuteriochloroform): δ 8.05 (d, 0.45H, Bt, minor isomer, J = 8.4 Hz), 8.02 (d, 0.55H, Bt, major isomer, J = 8.1 Hz), 7.63 (d, 1H, Bt, J = 8.4 Hz), 7.45 (m, 1H, Bt), 7.34 (m, 1H, Bt), 6.29 (m, 0.55H, CH=, major isomer), 6.11 (m, 0.45H, CH=, minor isomer), 5.95-5.74 (m, 2H, CH= and 1-H), 3.93 (m, 0.9H, OCH_2, minor isomer), 3.68 (m, 1.1H, OCH_2, major isomer), 3.31 (m, 0.45H, H-6, minor isomer), 3.15 (m, 0.55H, H-6, major isomer), 2.56-1.98 (m, 4H, $2CH_2$), 0.95 (t, 1.35H, CH_3, minor isomer), 0.86 (t, 1.65H, CH_3, major isomer); ^{13}C nmr (deuteriochloroform): δ 173.0 (C=O), 171.3 (C=O), 145.8, 145.5, 133.6, 133.4, 132.5, 130.9, 127.0, 127.0, 126.8, 126.8, 124.7, 123.7, 123.6, 122.2, 119.7, 119.6, 110.4, 110.0, 60.8 (OCH_2), 60.5 (OCH_2), 56.8 (C-1), 53.9 (C-1), 45.6 (C-6), 45.1 (C-6), 24.9 (CH_2), 24.3 (CH_2), 23.9 (CH_2), 19.5 (CH_2), 13.6 (CH_3), 13.4 (CH_3).

Anal. Calcd. for $C_{15}H_{17}N_3O_2$: C, 66.40; H, 6.32; N, 15.49. Found: C, 66.44; H, 6.34; N, 15.28.

2-(Benzotriazol-1-yl)-1,1-dimethyl-1,2,5,6-tetrahydropyridinium Iodide (**7**).

A suspension of butadiene **4a** (0.68 g, 4 mmoles) and Eschnomoser's salt (0.81 g, 4.4 mmoles) in anhydrous dichloromethane was stirred at 25° for 2 days. The precipitate was filtered, washed with chloroform, ethanol, and crystallized from ethanol to yield 1.1 g (77%) of **7**, mp 202-204°; ^{1}H nmr (dimethyl sulphoxide-d_6): δ 8.23 (d, 1H, Bt, J = 8.3 Hz), 8.14 (d, 1H, Bt, J = 8.2 Hz), 7.76 (dd, 1H, Bt, J = 7.5, 7.5 Hz), 7.57 (dd, 1H, Bt, J = 7.5, 7.5 Hz), 7.36 (s, 1H, 2-H), 6.48 (m, 1H, 3-H), 6.00 (dd, 1H, 4-H, J = 10.4, 1.4 Hz), 4.00-3.85 (m, 2H, N-CH_2), 3.34 (s, 3H, N-CH_3), 2.92 (s, 3H, N-CH_3), 2.73 (m, 2H, CH_2); ^{13}C nmr (dimethyl sulphoxide-d_6): δ 145.0, 134.1, 130.1, 129.3, 125.1, 120.0, 119.3, 111.2, 75.5 (C-2), 57.8 (C-6), 50.6 (CH_3), 45.4 (CH_3), 20.9 (C-5).

Anal. Calcd. for $C_{13}H_{17}N_4I$: C, 43.83; H, 4.81; N, 15.73. Found: C, 43.54; H, 4.81; N, 15.50.

6-(Benzotriazol-1-yl)-2-phenyl-3,6-dihydro-2*H*-1,2-oxazine (**8**).

A mixture of butadiene **4a** (0.1 g, 0.6 mmole) and nitrosobenzene (0.06 g, 0.6 mmole) in chloroform was stirred for 24 hours at 25°. The crude mixture was subjected to column chromatography (eluent; hexane-chloroform) to yield 0.15 g (90%) of **8**, mp 126°; ^{1}H nmr (deuteriochloroform): δ 8.02 (d, 1H, Bt, J = 8.3 Hz), 7.78 (d, 1H, Bt, J = 8.3 Hz), 7.42 (m, 1H, Bt), 7.35 (m, 1H, Bt), 7.21 (m, 2H, Ph), 6.91 (m, 3H, phenyl), 6.55 (m, 1H, 5-H), 6.27 (m, 1H, 4-H), 4.17-3.89 (m, 2H, CH_2); ^{13}C nmr (deuteriochloroform): δ 148.2, 146.4, 132.9, 129.7, 128.6, 127.5, 124.0, 123.2, 122.2, 119.7, 116.4, 111.8, 83.7 (C-6), 51.1 (C-2).

Anal. Calcd. for $C_{16}H_{14}N_4O$: C, 69.05; H, 5.07; N, 20.13. Found: C, 68.73; H, 5.10; N, 19.90.

General Procedure for the Preparation of Compounds **9a-d**.

Lithium diisopropylamide (LDA, 1.5 *M*) in cyclohexane (0.85 ml, 1.32 mmoles) was added dropwise to the appropriate butadiene **4a,b** (1.2 mmoles) in THF (20 ml) at -78°. The solution was stirred for 45 minutes at -78°, and the electrophile (1.2 mmoles) in THF (5 ml) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for an additional 4 hours. Aqueous 10% ammonium chloride was added, followed by extraction with chloroform (3 x 20 ml). The organic phase was washed with water (2 x 20 ml) and dried (magnesium sulfate). The solvent was evaporated, and the crude product purified by column chromatography (eluent: hexane-chloroform).

2-(Benzotriazol-1-yl)-1-hydroxy-1-phenylpenta-2,4-diene (**9a**).

This compound was obtained as an oil (65%); ^{1}H nmr (deuteriochloroform): δ 7.97 (d, 1H, Bt, J = 8.3 Hz), 7.48-7.00 (m, 9H, aromatic and 4-CH=), 6.59 (d, 1H, 3-H, J = 11.1 Hz), 6.29 (d, 1H, 1-H, J = 8.0 Hz), 5.56 (dd, 2H, CH_2, J = 7.8, 11.1 Hz), 4.66 (d, 1H, OH, J = 8.0 Hz); ^{13}C nmr (deuteriochloroform): δ 144.9, 140.1, 136.3, 133.0, 129.7, 128.2 (2C), 127.9, 127.5, 125.2, 124.3, 124.1, 119.8, 110.5, 71.0 (C-1).

Anal. Calcd. for $C_{17}H_{15}N_3O$: C, 73.63; H, 5.45; N, 15.15. Found: C, 73.75; H, 5.56; N, 15.36.

2-(Benzotriazol-1-yl)-1-hydroxy-1,1-diphenylpenta-2,4-dione (**9b**).

This compound was obtained in 70% yield as rods (chloroform), mp 155°; ^{1}H nmr (deuteriochloroform): δ 7.92 (d, 1H, Bt, J = 8.4 Hz), 7.55-7.19 (m, 13H, aromatic), 6.55 (d, 1H, 3-H, J = 11.4 Hz), 5.66 (m, 1H, 4-H), 5.29 (d, 1H, CH_AH_B, J = 16.8 Hz), 5.13 (d, 1H, CH_AH_B, J = 11.7 Hz); ^{13}C nmr (deuteriochloroform): δ 143.7, 138.4, 133.0, 130.5, 128.3, 128.2, 128.0, 127.9, 127.4, 126.5, 124.7, 124.0, 119.8, 110.6, 81.6 (C-1).

Anal. Calcd. for $C_{23}H_{19}N_3O$: C, 78.16; H, 5.42; N, 11.89. Found: C, 77.97; H, 5.41; N, 11.80.

2-(Benzotriazol-1-yl)-1-hydroxy-1,1,5-triphenylpenta-2,4-diene (**9c**).

This compound was obtained in 68% yield as grains (chloroform), mp 175-178°; ^{1}H nmr (deuteriochloroform): δ 7.96 (d, 1H,

Bt, J = 8.4 Hz), 7.60-6.92 (m, 18H, aromatic and 4-CH=), 6.69 (d, 1H, 5-H, J = 11.7 Hz), 6.51 (d, 1H, 3-H, J = 15.6 Hz), 5.85 (dd, 1H, 4-H, J = 15.6, 11.7 Hz); ^{13}C nmr (deuteriochloroform): δ 144.9, 143.8, 138.9, 137.4, 136.1, 133.9, 131.9, 128.6, 128.5, 128.3, 128.1, 128.1, 128.0, 127.6, 127.0, 124.2, 122.2, 120.0, 110.7, 81.7 (C-1).

Anal. Calcd. for $C_{29}H_{23}N_3O$: C, 81.09; H, 5.40; N, 9.78. Found: C, 80.78; H, 5.39; N, 9.76.

2-(Benzotriazol-1-yl)-1-(2,4-dichlorophenyl)-1-hydroxy-5-phenylpenta-2,4-diene (**9d**).

This compound was obtained in 69% yield as a colorless solid, mp 203-205°; ^{1}H nmr (deuteriochloroform): δ 8.01 (d, 1H, Bt, J = 8.4 Hz), 7.55-7.20 (m, 12H, aromatic and 4-CH=), 6.98 (dd, 1H, aromatic, J = 8.5, 2.2 Hz), 6.88 (d, 1H, 5-H, J = 11.4 Hz), 6.72 (d, 1H, 3-H, J = 11.3 Hz), 6.49 (d, 1H, 1-H, J = 7.0 Hz), 4.62 (d, 1H, OH, J = 7.0 Hz); ^{13}C nmr (deuteriochloroform): δ 144.3, 138.1, 136.8, 135.9, 134.4, 133.7, 132.8, 132.1, 131.4, 129.0, 128.5, 128.4, 128.1, 127.3, 126.6, 126.4, 123.5, 121.8, 118.7, 111.0, 67.2 (C-1).

Anal. Calcd. for $C_{23}H_{17}N_3Cl_2O$: C, 65.41; H, 4.06; N, 9.95. Found: C, 65.25; H, 4.08; N, 9.73.

X-Ray Crystallography of **7**.

Intensity data were collected at -90° with a Nicolet R3m four-circle diffractometer by using monochromatized MoKα (λ = 0.71073 Å) radiation. The crystal used was a colorless block of dimensions 0.25 x 0.24 x 0.10 mm. Cell parameters were determined by least squares refinement, the setting angles of 25 accurately centered reflections ($2\theta > 15°$) being used. Throughout data collections the intensities of three standard reflections were monitored at regular intervals and this indicated no significant crystal decomposition. The space group followed from systematic absences. The intensities were corrected for Lorentz and polarization effects but not for absorption. Reflections with $I > 3\sigma(I)$ were used for structure solution and refinement.

The structures were solved by direct methods, and refined by full-matrix least squares procedures. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were included in calculated positions with isotropic displacement coefficient equal to 1.2 times the isotropic equivalent of their carrier carbon. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$, with $w = [\sigma^2(F_o) + 0.0005F_o^2]^{-1}$. Final difference maps showed no features greater or less than 0.25e$^-$/Å^3. Final non-hydrogen atom coordinates, bond lengths and bond angles are listed in Tables 1 and 2. Tabulations of hydrogen atom coordinates, anisotropic thermal parameter, structure factors and equations of meanplanes are available as supplementary material from the author PJS.

Crystal data for the oxazine at -90° for $C_{16}H_{14}N_4O$ are Mr = 278.3, monoclinic, space group $p2_1/n$, a = 6.946 (2), b = 8.153 (3), c = 24.883 (13) Å, β = 94.82 (3)°, U = 1404(1) Å^3, F(000) = 584, Z = 4, D_c = 1.316 g cm^{-3}, μ (Mo-Kα) = 0.81 cm^{-1}, ω scans, $2\theta_{max}$ = 48°, N = 2200, N_o = 1449, 190 parameters, S = 1.17, R = 0.037, R_w = 0.042.

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