Synthesis and Reactions of Lithio Derivatives of 1-Allenylbenzotriazole

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1-(2-Chloropropen-2-yl)benzotriazole (**6**) is converted by heating with sodium hydroxide or by lithium diisopropylamide at -78° into 1-allenylbenzotriazole (**1**) in high yield. Allene **1** undergoes *in situ* lithiation at the α-carbon and subsequent reactions with iodomethane or carbonyl compounds to produce 1-(1-substituted allenyl)benzotriazoles **9** and **2a-c**, respectively. Three equivalents of lithium diisopropylamide dilithiated **1** and afforded symmetrical 1-(1,3-disubstituted allenyl)benzotriazoles **11a,b** upon reaction with ketones. The unsymmetrical 1-(1,3-disubstituted allenyl)benzotriazole **5** was obtained *via* a stepwise addition of benzophenone to the lithio derivative of **1** followed by a second lithiation and quenching with acetone. Monosubstituted allenes **2a** and **8** were cyclized into the benzotriazolyl substituted dihydrofuran **3** and dihydropyrrole **4** respectively.

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Hetero substituted allenes have attracted a growing attention because of their biological activity and their versatility as key building blocks for organic synthesis. For example, in the last two decades they were successfully used for the preparation of numerous heterocycles such as pyrans [1-4], isoxazolidines [5], spiroisoxazolidines [6], diazoles [7], dihydrooxazines [8,9], dihydropyridines [10,11], octahydroindolizines [12], benzoazepinones [13], dihydrofuranones [14] and fused furans [15], mostly *via* hetero Diels-Alder reactions with inverse electron demand. Due to their high reactivity, hetero substituted allenes could potentially be involved in a number of transformations, but their main synthetic use presently is based on their ability to undergo heteroatom assisted lithiation and subsequent reactions with various electrophiles [16-19].

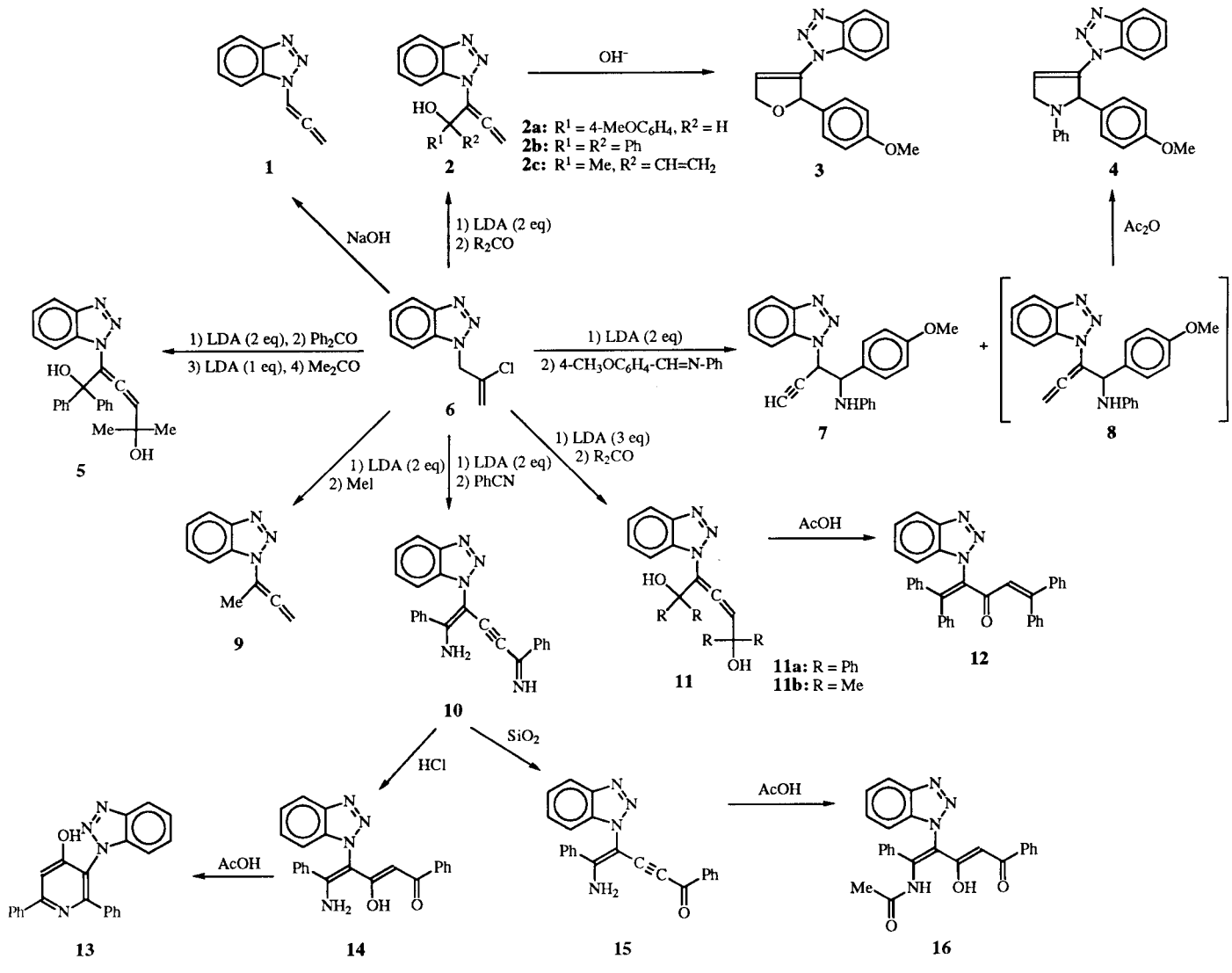
Despite this, there are only a few examples in the literature detailing the preparation of allenes substituted with heteroaromatic rings. These include the alkylation of nitroimidazoles with propargyl bromide to yield *N*-propargyl or *N*-allenyl derivatives with high chemo selectivity [20]. Similarly, the formation of 2-allenylbenzotriazole was observed in the alkylation reaction of benzotriazole with propargyl bromide, but 1-propargylbenzotriazole was the major product [21]. Trofimov and co-workers reported a further method in which they obtained *N*-allenylpyrroles by treatment of the corresponding bases with 2,3-dichloro-1-propene in potassium hydroxide/dimethyl sulfoxide [22,23].

In this paper we report that a variety of benzotriazolyl substituted allenes and their derivatives are available from 1-(2-chloropropen-2-yl)benzotriazole (**6**). The starting material **6** was prepared by alkylation of benzotriazole with 2,3-dichloro-1-propene in dimethyl sulfoxide in the presence of sodium carbonate. This reaction produced a mixture of **6** (56%) and the isomeric 2-(2-chloropropen-2-yl)benzotriazole (30%). Treatment of the mixture with hexane caused precipitation of crystalline **6**, thus affording separation. Briefly boiling a solution of **6** in dimethyl sulfoxide in the presence of sodium hydroxide afforded 1-allenylbenzotriazole **1** in 90% yield by elimination of hydrochloric acid.

Treatment of **6** with lithium diisopropylamide or butyllithium also resulted in the elimination of hydrochloric acid and allene **1**, generated *in situ*, underwent α-lithiation on addition of a second equivalent of lithiating agent. Quenching of the lithioderivative of **1** with iodomethane resulted in the formation of 1-(1-methylallenyl)benzotriazole **9** in 86% yield. Similarly, the reactions of **6** with two equivalents of lithium diisopropylamide followed by *p*-methoxybenzaldehyde or benzophenone gave the expected alcohols **2a,b** in 90% and 66% yields, respectively. Interestingly, alcohol **2c** was obtained in 73% yield when methyl vinyl ketone was the carbonyl source, and no Michael addition product was observed.

By comparison, treatment of **6** with two equivalents of lithium diisopropylamide followed by addition of *N*-(4-methoxybenzylidene)aniline to the reaction mixture gave the rearrangement product, propargyl derivative **7**, in 43% yield.

Surprisingly, it was found that the reaction of **6** with two equivalents of lithium diisopropylamide followed by an excess of benzonitrile gave a product of bis-addition and rearrangement in 64% yield as a mixture of isomers **10**. A possible reaction mechanism involves the amide nitrogen of the initial benzonitrile adduct deprotonating the terminal carbon to form a carbanion, which reacts with the second equivalent of benzonitrile. Our attempted purification of compound **10** on silica gel afforded derivative **15**. Meanwhile, the treatment of **10** with aqueous hydrochloric acid gave product **14**. Interestingly, recrystallization of **15** from acetic acid produces **16**, apparently *via* addition of acetic acid to the triple bond and a subsequent intramolecular shift of the acetyl group to the nitrogen atom.



Treatment of **6** with three equivalents of lithium diisopropylamide followed by addition of an excess of benzophenone or acetone gave the products of bis-addition **11a,b** in 73% and 68% yields, respectively. These results suggest that the 1,3-dilithio derivative of **1** is generated in solution from **6** in the presence of a sufficient quantity of lithiating agent.

One could suggest that if one reaction center in the 1,3-dilithio derivative of **1** is more active than the other, it would be possible to obtain 1,3-unsymmetrically substituted 1-allenylbenzotriazoles *via* stepwise addition of two different electrophiles. In order to test this hypothesis, compound **6** was treated with three equivalents of lithium diisopropylamide and quenched with one equivalent of *p*-methoxybenzaldehyde. Unfortunately, this reaction afforded a mixture of products. This demonstrates that the two reaction centers of the dilithio derivative of **1** have similar reactivities.

However, the target 1,3-unsymmetrically substituted 1-allenylbenzotriazole **5** was obtained in a stepwise one-pot procedure. Starting material **6** was treated with two equivalents of lithium diisopropylamide followed by the addition of one equivalent of benzophenone. After stirring the reaction mixture for one hour at -78° the second lithiation with one equivalent of lithium diisopropylamide was undertaken. Subsequent addition of an excess of acetone afforded the allene **5** in 46% yield.

Allenyl substituents attached to the benzotriazole ring may be converted into various heterocyclic systems. Thus, when the reaction mixture obtained after separation of propargyl derivative **7** is heated briefly in acetic anhydride, dihydropyrrole **4** is obtained in 30% yield. This compound is presumably derived from allenyl derivative **8**, as compound **7** does not cyclize under these conditions. The related dihydrofuran derivative **3** was obtained from the reaction of allene **2a** with alkali in 60% yield.

Likewise, compound **14** quantitatively undergoes cyclization into 4-hydroxypyridine derivative **13** on prolonged heating in acetic acid. However, on attempting to convert disubstituted allene **11a** into the tetrahydro-γ-pyrone derivative, chalcone **12** was obtained.

In contrast to the successful conversion of compound **6** into various 1-allenylbenzotriazoles, we failed to obtain either 2-allenylbenzotriazole or its derivatives in a pure state from 2-(2-chloropropen-2-yl)benzotriazole. This may be a result of the recently discovered ability of 2-substituted benzotriazoles to rapidly undergo radical reactions [24,25]

EXPERIMENTAL

Melting points were determined with a hot stage apparatus and are uncorrected. ^1H and ^{13}C nmr spectra were recorded on a Varian VXR-300 (300 MHz) spectrometer using TMS as an internal standard. Elemental analyses were performed by this Department. Column chromatography was carried out using silica gel (230-400 mesh).

1-(2-Chloropropen-2-yl)benzotriazole (**6**) and 2-(2-Chloropropen-2-yl)benzotriazole.

To a mixture of 90 ml of dimethyl sulfoxide, 20 ml of water, 19.1 g (0.18 mole) of sodium carbonate and 9.5 g (0.08 mole) of benzotriazole 12 ml (0.13 mole) of 2,3-dichloro-1-propene was added dropwise at 20° and the mixture was stirred at room temperature for 16 hours. The reaction mixture was poured onto 400 g of ice and extracted with 200 ml of toluene. The toluene solution was separated, dried with magnesium sulfate and the solvent evaporated *in vacuo* to give a white sticky solid. This residue was heated to boiling with 70 ml of hexane and left at room temperature overnight. The resulting white solid was collected and air-dried to yield 8.7 g (56%) of **6**, mp 112-114°; ^1H nmr (deuteriochloroform): δ 5.28-5.30 (m, 1H, alkene proton), 5.41-5.42 (m, 2H, $-CH_2-$), 5.46-5.47 (m, 1H, alkene proton), 7.4-7.6 (m, 3H, 5-, 6-, and 7-H), 8.07 (d, 1H, 4-H, J = 8.3 Hz); ^{13}C nmr (deuteriochloroform): δ 53.6, 109.4, 115.9, 115.9, 120.0, 124.1, 127.7, 132.8, 134.8, 145.9.

Anal. Calcd. for $C_9H_8ClN_3$: C, 55.83; H, 4.16; N, 21.70. Found: C, 55.94; H, 4.37; N, 21.65.

The mother liquor obtained after separation of **6** was evaporated to yield 4.6 g (30%) of 2-(2-chloropropen-2-yl)benzotriazole as an oil; ^1H nmr (deuteriochloroform): δ 5.32-5.33 (m, 1H, alkene proton), 5.38 (br s, 2H, CH_2), 5.42-5.43 (m, 1H, alkene proton), 7.27-7.30 (m, 2H, 5- and 6-H), 7.77-7.81 (m, 2H, 4- and 7-H); ^{13}C nmr (deuteriochloroform): δ 61.7, 117.1, 118.1, 126.7, 134.6, 144.6.

Anal. Calcd. for $C_9H_8ClN_3$: C, 55.83; H, 4.16; N, 21.70. Found: C, 55.98; H, 4.12; N, 21.75.

1-Allenylbenzotriazole (**1**).

To a solution of 0.1 g (0.5 mmole) of 1-(2-chloropropen-2-yl)benzotriazole (**6**) in 1 ml of dimethyl sulfoxide, 0.11 ml of a 20% aqueous solution of sodium hydroxide (1 mmole) was added. The mixture was rapidly heated to boiling, cooled and 10 ml of cool water was added. After 2 hours, the solid product was filtered and air-dried to yield 0.08 g (90%) of **1**, mp 64-66°; ^1H nmr (deuteriochloroform): δ 5.82 (d, 2H, allene protons, J = 6.6 Hz), 7.39-7.51 (m, 2H, allenyl proton and 5-H), 7.81-7.87 (m, 2H, 6-H and 7-H), 8.07 (d, 1H, 4-H, J = 8.3 Hz); ^{13}C nmr (deuteriochloroform): δ 88.8, 97.9, 110.9, 120.0, 124.5, 127.8, 131.5, 146.4, 201.7.

Anal. Calcd. for $C_9H_7N_3$: C, 68.78; H, 4.49; N, 26.73. Found: C, 68.39; H, 4.55; N, 26.76.

General Procedure for the Generation *in situ* of 1-(1-Lithioallen-1-yl)benzotriazole and Subsequent Reactions with Various Electrophiles.

All of these reactions were carried out under a nitrogen atmosphere. To a stirred and cooled (-78°) solution of 1-(2-chloropropen-2-yl)benzotriazole (**6**) (0.39 g, 2 mmoles), 2.8 ml of a 1.5 *M* solution (4.2 mmoles) of lithium diisopropylamide in cyclohexene was added dropwise. The mixture was stirred for 15 minutes at -78° before the addition of the corresponding electrophile.

1-(α-Hydroxy-4-methoxybenzylallen-1-yl)benzotriazole (**2a**).

This compound was obtained using 4-methoxybenzaldehyde (0.4 ml, 3.2 mmoles) as the electrophile. Dropwise addition of the electrophile to the reaction mixture was followed by stirring at -78° for 40 minutes and subsequent quenching with 1.5 ml of water. The mixture was allowed to warm to room temperature and poured into 20 ml of water, then extracted with 15 ml of ethyl acetate. The solvent was evaporated *in vacuo* and the residue was separated by column chromatography (silica gel, chloroform) to give 0.51 g (90%) of colorless needles (ether), mp 109-111°; ^1H nmr (deuteriochloroform): δ 3.73 (s, 3H, OCH_3), 4.31 (br s, 1H, OH), 5.61 (s, 2H, allenyl), 6.19 (d, 1H, CH, J = 5.4 Hz), 6.80 (d, 2H, phenyl, J = 8.7 Hz), 7.32-7.49 (m, 4H, 5-H, 6-H and phenyl), 7.69 (d, 1H, 7-H, J = 8.7 Hz), 8.01 (d, 1H, 4-H, J = 8.7 Hz); ^{13}C nmr (deuteriochloroform): δ 55.1, 72.7, 88.3, 111.2, 113.1, 113.5, 119.9, 124.6, 127.8, 128.0, 131.7, 132.4, 145.5, 159.2, 201.3.

Anal. Calcd. for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33. Found: C, 69.35; H, 5.12; N, 14.30.

1-(1-Hydroxydiphenylmethylallen-1-yl)benzotriazole (**2b**).

This compound was obtained using benzophenone (0.45 g, 2.5 mmoles) in a solution of 4 ml of tetrahydrofuran as the electrophile. After dropwise addition of this solution, the reaction mixture was stirred at -78° for 1 hour, then quenched with 1.5 ml of water. The mixture was allowed to warm to room temperature, poured into 20 ml of water and extracted with 15 ml of ethyl acetate. The solvent was evaporated *in vacuo* and the residue was separated by column chromatography (silica gel, chloroform) to give 0.46 g (66%) of colorless plates (hexane), mp 116-118°; ^1H nmr (deuteriochloroform): δ 5.33 (s, 2H, allenyl), 6.00 (s, 1H, OH), 7.19-7.27 (m, 6H, phenyl), 7.39 (t, 1H, 5-H, J = 8.2 Hz), 7.46-7.51 (m, 4H, phenyl), 7.54 (t, 1H, 6-H, J = 8.2 Hz), 7.79 (d, 1H, 7-H, J = 8.2 Hz), 8.01 (d, 1H, 4-H, J = 8.2 Hz); ^{13}C nmr (deuteriochloroform): δ 82.1, 87.6, 111.0, 114.6, 120.3, 124.7, 127.0, 127.2, 127.6, 127.7, 127.9, 128.4, 132.7, 143.2, 145.0, 202.9.

Anal. Calcd. for $C_{22}H_{17}N_3O$: C, 77.86; H, 5.05; N, 12.38. Found: C, 77.99; H, 5.06; N, 12.41.

1-(1-Hydroxy-1-vinylethylallen-1-yl)benzotriazole (**2c**).

This compound was obtained using methylvinyl ketone (0.16 g, 2.3 mmoles) in a solution of 4 ml of tetrahydrofuran as the electrophile. After dropwise addition of this solution, the reac-

tion mixture was stirred at -78° for 30 minutes, then quenched with 1.5 ml of water. The mixture was allowed to warm to room temperature, poured into 20 ml of water and extracted with 15 ml of ethyl acetate. The solvent was evaporated *in vacuo* and the residue was separated by column chromatography (silica gel, chloroform) to give 0.33 g (73%) of a colorless oil; ^{1}H nmr (deuteriochloroform): δ 1.60 (s, 3H, CH_3), 4.78 (s, 1H, OH), 5.02 (dd, 1H, vinyl, J = 10.6, 0.8 Hz), 5.34 (dd, 1H, vinyl, J = 17.2, 0.8 Hz), 5.68 (d, 1H, allenyl, J = 12.2 Hz), 5.74 (d, 1H, allenyl, J = 12.2 Hz), 5.98 (dd, 1H, vinyl, J = 17.2, 10.6 Hz), 7.41-7.44 (m, 1H, 5-H), 7.50-7.55 (m, 1H, 6-H), 7.67 (d, 1H, 7-H, J = 8.4 Hz), 8.09 (d, 1H, 4-H, J = 8.2 Hz); ^{13}C nmr (deuteriochloroform): δ 26.8, 74.3, 87.4, 110.9, 114.4, 114.5, 120.1, 124.6, 128.2, 133.1, 141.6, 145.0, 201.6.

Anal. Calcd. for $C_{13}H_{13}N_3O$: C, 68.71; H, 5.77; N, 18.49. Found: C, 69.02; H, 5.97; N, 18.57.

1-(1-Methylallen-1-yl)benzotriazole (**9**).

This compound was obtained using iodomethane (0.22 ml, 3.5 mmoles) as the electrophile. After this reagent was added dropwise, the reaction mixture was stirred at -78° for 40 minutes and was then quenched with 1.5 ml of water. The mixture was allowed to warm to room temperature, poured into 20 ml of water and extracted with 15 ml of ethyl acetate. The solvent was evaporated *in vacuo* and the residue separated by column chromatography (silica gel, toluene) to give 0.30 g (86%) of colorless needles (hexane), mp 47-48°; ^{1}H nmr (deuteriochloroform): δ 2.61 (t, 3H, CH_3, J = 3.1 Hz), 5.60 (q, 2H, allenyl, J = 3.1 Hz), 7.37 (t, 1H, 6-H, J = 7.8 Hz), 7.46 (t, 1H, 5-H, J = 7.8 Hz), 7.85 (d, 1H, 7-H, J = 7.8 Hz), 8.06 (d, 1H, 4-H, J = 7.8 Hz); ^{13}C nmr (deuteriochloroform): δ 18.0, 86.0, 106.8, 111.6, 119.8, 124.2, 127.4, 132.0, 146.3, 201.7.

Anal. Calcd. for $C_{10}H_9N_3$: C, 70.16; H, 5.30; N, 24.54. Found: C, 69.89; H, 5.30; N, 24.75.

3-(Benzotriazol-1-yl)-4-aminophenyl-4-(4-methoxyphenyl)but-1-yne (**7**) and 1-Phenyl-2-(4-methoxyphenyl)-3-(benzotriazol-1-yl)-2,5-dihydropyrrole (**4**).

This compound was obtained using *N*-(4-methoxybenzyliden)aniline (0.47 g, 2.2 mmoles) in a solution of 4 ml of tetrahydrofuran as the electrophile. After dropwise addition of this solution the reaction mixture was stirred at -78° for 80 minutes and was then quenched with 1.5 ml of water. The mixture was allowed to warm to room temperature, poured into 20 ml of water and extracted with 15 ml of ethyl acetate. The solvent was evaporated *in vacuo* and the residue separated by column chromatography (silica gel, chloroform) to give two main fractions, the second of which contained 0.31 g (43%) of pure **7** as colorless needles (2-propanol), mp 181-184°; ^{1}H nmr (deuteriochloroform): δ 2.80 (d, 1H, ethynyl, J = 2.6 Hz), 3.71 (s, 3H, OCH_3), 4.85 (d, 1H, NH, J = 6.4 Hz), 5.00 (dd, 1H, NCH, J = 6.4, 4.7 Hz), 6.15 (dd, 1H, propargyl, J = 4.7, 2.6), 6.51 (d, 2H, phenyl, J = 8.5 Hz), 6.63-6.71 (m, 3H, phenyl), 7.02-7.08 (m, 4H, phenyl), 7.29-7.37 (m, 3H, 5-H, 6-H, 7-H), 7.99-8.02 (m, 1H, 4-H); ^{13}C nmr (deuteriochloroform): δ 55.2, 57.6, 61.6, 75.9, 78.1, 110.9, 114.0 (2C), 118.4, 119.9, 124.0, 127.4, 128.2, 129.1, 129.1, 132.7, 145.9, 146.0, 159.6.

Anal. Calcd. for $C_{23}H_{20}N_4O$: C, 74.98; H, 5.47; N, 15.21. Found: C, 74.79; H, 5.52; N, 15.27.

The first fraction obtained from the column, after evaporation of the solvent, was refluxed in 3 ml of acetic anhydride for 5 minutes, then hydrolyzed with 20 ml of water overnight at room temperature. The oil obtained was purified by column chromatography (silica gel, chloroform) to give 0.21 g (30%) of compound **4** as colorless plates (2-propanol), mp 158°; ^{1}H nmr (deuteriochloroform): δ 3.63 (s, 3H, OCH_3), 4.57 (ddd, 1H, CH_2, J = 14.6, 2.7, 2.6 Hz), 4.81 (ddd, 1H, CH_2, J = 14.6, 6.6, 1.9 Hz), 6.29-6.32 (m, 1H, 4-H of pyrrole), 6.33-6.38 (m, 1H, CH), 6.65-6.73 (m, 5H, phenyl), 7.17-7.25 (m, 2H, phenyl), 7.33-7.38 (m, 3H, phenyl and 5-H), 7.46-7.52 (m, 1H, 6-H), 7.60 (d, 1H, 7-H, J = 8.1 Hz), 8.02 (d, 1H, 4-H, J = 8.3 Hz); ^{13}C nmr (deuteriochloroform): δ 54.3, 55.0, 67.4, 110.5, 111.8, 112.2, 113.9, 116.7, 120.3, 124.5, 128.3, 128.6, 129.2, 131.7, 132.3, 138.4, 145.4, 145.9, 159.0.

Anal. Calcd. for $C_{23}H_{20}N_4O$: C, 74.98; H, 5.47; N, 15.21. Found: C, 75.11; H, 5.53; N, 15.23.

1-Amino-2-(benzotriazol-1-yl)-2-iminobenzoylethynylstyrene (**10**).

This compound was obtained using benzonitrile (0.52 g, 5 mmoles) in a solution of 4 ml of tetrahydrofuran as the electrophile. After this solution was added dropwise, the reaction mixture was stirred at -78° for 5 minutes then allowed to warm gradually to room temperature overnight. The mixture was poured into 30 ml of water, extracted with 30 ml of ethyl acetate, dried over magnesium sulfate and the solvent evaporated *in vacuo*. The residue was washed with 20 ml of ether to give 0.48 g (64%) of a brown solid, mp 157-160°; ^{1}H nmr [(dimethyl sulfoxide-d_6), mixture of isomers]: δ 7.06 (br s, 2H, NH_2), 7.13-7.29 (m, 2H, phenyl), 7.30-7.75 (m, 8H, phenyl, 5-H and 6-H), 7.78-8.01 (m, 3H, phenyl and 7-H), 8.19 (d, 1H, 4-H, J = 8.1 Hz), 10.15 (br s, 1H, NH); ^{13}C nmr [(dimethyl sulfoxide-d_6), mixture of isomers]: δ 83.3, 84.2, 88.4, 90.2, 93.8, 94.2, 110.0, 110.3, 118.9, 119.2, 123.6, 123.7, 126.4, 127.0 127.5, 127.7, 128.0, 128.3, 128.7, 129.8, 130.3, 130.6, 131.9, 133.1, 133.6, 133.7, 134.8, 136.2, 144.1, 144.9, 156.4, 158.7, 158.7, 159.8; ms: m/z 363 (M^+).

Anal. Calcd. for $C_{23}H_{17}N_5$: C, 76.01; H, 4.71; N, 19.27. Found: C, 76.35; H, 4.74; N, 19.24.

1-Amino-2-(benzotriazol-1-yl)-2-benzoylethynylstyrene (**15**).

This compound was obtained using benzonitrile (0.52 g, 5 mmoles) in a solution of 4 ml of tetrahydrofuran as the electrophile. After this solution was added dropwise the reaction mixture was stirred at -78° for 5 minutes then allowed to warm gradually to room temperature overnight. The mixture was poured into 30 ml of water and extracted with 30 ml of ethyl acetate. The solvent was evaporated *in vacuo* and the residue separated by column chromatography (silica gel, chloroform) to give 0.31 g (42%) of yellow plates (isopropanol), mp 193-195°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 7.26-7.34 (m, 4H, NH_2 and phenyl), 7.48-7.57 (m, 3H, phenyl), 7.62-7.80 (m, 5H, phenyl), 7.90-8.00 (m, 3H, 5-H, 6-H and 7-H), 8.20 (d, 1H, 4-H, J = 8.0 Hz); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 84.0, 94.9, 100.0, 110.2, 119.3, 123.8, 127.7, 127.7, 128.1, 128.4, 128.8, 130.3, 132.9, 133.2, 134.2, 136.2, 144.9, 162.8, 174.5; ms: m/z 364 (M^+).

Anal. Calcd. for $C_{23}H_{16}N_4O$: C, 75.81; H, 4.43; N, 15.37. Found: C, 75.73; H, 4.44; N, 15.42.

1-Amino-1-phenyl-2-(benzotriazol-1-yl)-3-hydroxy-4-benzoyl-1,3-butadiene (**14**).

To a solution of **10** (0.18 g, 0.5 mmole) in ethanol (2 ml), 35% aqueous hydrochloric acid (0.2 ml) was added and the mix-

ture heated under reflux for 3 minutes. The solution was then cooled and 15 ml of water added. A white solid was collected and air-dried to yield 0.17 g (90%) of **15**, mp 193-195° (ethanol); ^{1}H nmr (deuteriochloroform): δ 7.09-7.44 (m, 10H, phenyl and NH_2), 7.51-7.59 (m, 3H, 5-H, 6-H and 7-H), 8.02 (s, 1H, =CH), 8.08-8.21 (m, 3H, 4-H and phenyl); ^{13}C nmr (deuteriochloroform): δ 109.4, 120.1, 120.2, 124.2, 126.8, 127.3, 128.1, 128.2, 128.5, 129.0, 129.3, 130.4, 133.9, 136.5, 136.9, 144.3, 145.4, 157.9, 159.2; ms: m/z 382 (M^+).

Anal. Calcd. for $C_{23}H_{18}N_4O_2$: C, 72.24; H, 4.74; N, 14.65. Found C, 72.32; H, 4.93; N, 14.33.

2,6-Diphenyl-3-(benzotriazol-1-yl)-4-hydroxypyridine (**13**).

A solution of **14** (0.19 g, 0.5 mmole) in acetic acid (2 ml) was heated under reflux for 14 hours, cooled and diluted with 15 ml of water. The white solid was collected and air-dried to yield 0.16 g (88%) of **13**, mp 284-286°; ^{1}H nmr (dimethyl sulfoxide-d_6, 120°): δ 7.09-7.21 (m, 3H), 7.21-7.29 (m, 2H), 7.32-7.58 (m, 8H), 7.98-8.10 (m, 3H); ^{13}C nmr (dimethyl sulfoxide-d_6, 120°): δ 110.0, 118.8, 123.3, 126.7, 127.3 (? 2C), 127.4, 127.5, 127.5 (? 2C), 127.6, 127.6, 128.2, 128.3 (? 2C), 129.3, 134.3 (? 2C), 144.6; ms: m/z 364 (M^+).

Anal. Calcd. for $C_{23}H_{16}N_4O$: C, 75.81; H, 4.43; N, 15.37. Found: C, 76.16; H, 4.44; N, 15.46.

1-Aminoacetyl-1-phenyl-2-(benzotriazol-1-yl)-3-hydroxy-4-benzoyl-1,3-butadiene (**16**).

A solution of **15** (0.18 g, 0.5 mmole) in acetic acid (2 ml) was heated under reflux for 3 minutes, cooled and 15 ml of water added. A pale yellow solid was collected, air-dried and crystallized from ethanol to yield 0.16 g (76%), mp 219-221°; ^{1}H nmr (deuteriochloroform): δ 2.26 (s, 3H, CH_3), 5.11 (s, 1H, =CH), 6.99-7.48 (m, 14H), 7.93 (d, 1H, 4-H, J = 8.0 Hz), 12.62 (s, 1H, NH); ^{13}C nmr (deuteriochloroform): δ 25.4, 93.5, 109.5, 112.7, 119.8, 124.0, 126.6 (2C), 127.5, 128.1, 128.5, 129.2, 131.4, 132.5, 132.8, 134.7, 144.9, 155.9, 168.1, 178.7, 190.5; ms: m/z 424 (M^+).

Anal. Calcd. for $C_{25}H_{20}N_4O_3$: C, 70.74; H, 4.75; N, 13.20. Found: C, 70.45; H, 4.44; N, 13.20.

1-[1,3-Di(1-hydroxy-1-phenylbenzyl)allenyl]benzotriazole (**11a**).

To a stirred and cooled (-78°) solution of 1-(2-chloropropen-2-yl)benzotriazole (**6**) (0.39 g, 2 mmoles) under nitrogen, 4.3 ml of a 1.5 *M* solution (6.4 mmoles) of lithium diisopropylamide in cyclohexene was added dropwise. The mixture was stirred for 15 minutes at -78°, then a solution of 0.9 g (5 mmoles) of benzophenone in 6 ml of tetrahydrofuran was added dropwise. The reaction mixture was stirred at -78° for 30 minutes, for 2 hours at room temperature, then quenched with 3 ml of water. The solution was poured into 30 ml of water and extracted with 30 ml of ethyl acetate. The solvent was evaporated *in vacuo* and the residue separated by column chromatography (silica gel, chloroform) to give 0.76 g (73%) of colorless plates (ether), mp 184-186°; ^{1}H nmr (deuteriochloroform): δ 2.41 (s, 1H, OH), 6.11 (s, 1H, OH), 6.43 (s, 1H, allenyl), 6.75-6.78 (m, 2H), 7.16-7.33 (m, 16H), 7.43-7.47 (m, 4H), 7.66 (d, 1H, 7-H, J = 8.3 Hz), 7.90 (d, 1H, 4-H, J = 8.3 Hz); ^{13}C nmr (deuteriochloroform): δ 78.1, 82.6, 111.5, 112.1, 118.1, 119.8, 124.7, 126.3, 126.8, 127.0, 127.6, 127.7, 127.8, 127.9, 127.9, 128.0, 128.1 (2C), 128.3, 128.3, 132.5, 143.4, 143.6, 143.7, 144.7, 144.8, 196.0.

Anal. Calcd. for $C_{35}H_{27}N_3O_2$: C, 80.59; H, 5.22; N, 8.06. Found: C, 80.19; H, 5.21; N, 7.99.

1-[1,3-Di(1-hydroxy-1-methylethyl)allenyl]benzotriazole (**11b**).

To a stirred and cooled (-78°) solution of 1-(2-chloropropen-2-yl)benzotriazole (**6**) (0.39 g, 2 mmoles) under nitrogen, 4.3 ml of a 1.5 *M* solution (6.4 mmoles) of lithium diisopropylamide in cyclohexene was added dropwise. The mixture was stirred for 15 minutes at -78°, then 0.37 ml (5 mmoles) of acetone was added. The reaction mixture was stirred at -78° for a further 40 minutes and was then quenched with 1.5 ml of water. The mixture was allowed to warm to room temperature, poured into 20 ml of water and extracted with 20 ml of ethyl acetate. The solvent was evaporated *in vacuo* and the residue separated by column chromatography (silica gel, chloroform) to give 0.47 g (68%) of colorless needles (hexane), mp 52-55°; ^{1}H nmr (deuteriochloroform): δ 1.42 (s, 6H, 2 CH_3), 1.48 (s, 3H, CH_3), 1.55 (s, 3H, CH_3), 3.94 (s, 1H, OH), 4.71 (s, 1H, OH), 6.14 (s, 1H, allenyl), 7.35-7.47 (two t, 2H, 5-H and 6-H, J = 8.1 Hz), 7.80 (d, 1H, 7-H, J = 8.3 Hz), 8.01 (d, 1H, 4-H, J = 8.3 Hz); ^{13}C nmr (deuteriochloroform): δ 28.3, 28.5, 29.6, 29.8, 70.2, 72.0, 111.4, 111.8, 117.1, 119.5, 124.4, 128.0, 133.5, 144.8, 193.8.

Anal. Calcd. for $C_{15}H_{19}N_3O_2$: C, 65.90; H, 7.01; N, 15.37. Found: C, 66.22; H, 7.17; N, 15.28.

1-[1-(1-hydroxy-1-phenylbenzyl)-3-(1-hydroxy-1-methylethyl)-allenyl]benzotriazole (**5**).

To a stirred and cooled (-78°) solution of 1-(2-chloropropen-2-yl)benzotriazole (**6**) (0.39 g, 2 mmoles) under nitrogen, 2.8 ml of a 1.5 *M* solution (4.2 mmoles) of lithium diisopropylamide in cyclohexene was added dropwise. The mixture was stirred for 15 minutes at -78°, after which a solution of 0.37 g (2 mmoles) of benzophenone in 4 ml of tetrahydrofuran was added dropwise. The reaction mixture was stirred at -78° for a further hour before the dropwise addition of 1.4 ml of a 1.5 *M* solution (2.1 mmoles) of lithium diisopropylamide in cyclohexene. The mixture was stirred for 15 minutes at -78°, then 0.2 ml of acetone was added dropwise. The mixture was stirred for 20 minutes at -78°, then quenched with 2 ml of water. The mixture was allowed to warm to room temperature, poured into 20 ml of water and extracted with 20 ml of ethylacetate. The solvent was evaporated *in vacuo* and the residue was separated by column chromatography (silica gel, chloroform) to give 0.36 g (46%) of colorless plates (hexane), mp 123-125°; ^{1}H nmr (deuteriochloroform): δ 1.07 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.31 (s, 1H, OH), 5.81 (s, 1H, allenyl), 6.06 (s, 1H, OH), 7.21-7.29 (m, 6H), 7.39-7.57 (m, 6H), 7.95 (d, 1H, 7-H, J = 7.5 Hz), 8.12 (d, 1H, 4-H, J = 7.5 Hz); ^{13}C nmr (deuteriochloroform): δ 28.8, 29.4, 70.1, 82.4, 111.5, 112.5, 116.6, 120.2, 124.8, 127.1, 127.2, 127.7, 127.7, 128.0, 128.0, 128.5, 132.7, 143.6, 143.8, 145.0, 194.7.

Anal. Calcd. for $C_{25}H_{23}N_3O_2$: C, 75.35; H, 5.83; N, 10.57. Found: C, 75.36; H, 5.86; N, 10.48.

2,2,2',2'-Tetraphenyl-1-(benzotriazol-1-yl)divinyl ketone (**12**).

A solution of **11a** (0.25 g, 0.5 mmole) in acetic acid (3 ml) was heated under reflux for 80 minutes, cooled and 15 ml of water were added. A yellow solid was collected, air-dried and separated by column chromatography (silica gel, chloroform) to yield yellow prisms 0.13 g (54%), mp 196-198° (isopropanol); ^{1}H nmr (deuteriochloroform): δ 6.33 (s, 1H, =CH), 6.55-6.57 (m, 2H), 6.71-6.74 (m, 2H), 6.87-7.18 (m, 5H), 7.23-7.55 (m, 14H), 7.90-7.94 (m, 1H, 4-H); ^{13}C nmr (deuteriochloroform): δ 109.9, 119.7, 123.7, 126.0, 127.3, 127.8, 127.8, 127.9, 128.1, 128.3, 128.5, 128.7, 128.9, 129.2, 129.3, 129.6, 130.5, 130.5,

131.3, 133.1, 138.2, 139.3, 141.4, 145.0, 148.9, 154.0, 190.3.

Anal. Calcd. for $C_{35}H_{25}N_3O$: C, 83.48; H, 5.00; N, 8.34. Found: C, 83.29; H, 5.03; N, 8.29.

1-(4-Methoxyphenyl)-2-(benzotriazol-1-yl)-2,4-dihydrofuran (**3**).

To a solution of **2a** (0.20 g, 0.75 mmole) in ethanol (2 ml) 35% aqueous sodium hydroxide (0.3 ml) was added and the mixture heated to boiling, cooled and 15 ml of water added. A white solid was collected, air-dried and recrystallized from ethanol to yield 0.12 g (60%), mp 136-138°; ^{1}H nmr (deuteriochloroform): δ 3.70 (s, 3H, OCH_3), 5.16 (ddd, 1H, -CH_2-, J = 13.4, 3.1, 1.9 Hz), 5.21 (ddd, 1H, -CH_2-, J = 13.4, 5.9, 1.7 Hz), 6.41 (ddd, 1H, CH, J = 1.9, 1.7, 1.7 Hz), 6.59 (ddd, 1H, =CH, J = 5.9, 3.1, 1.7 Hz), 6.74-6.78 (m, 2H, phenyl), 7.32-7.41 (m, 3H, phenyl and 5-H), 7.51-7.56 (m, 1H, 6-H), 7.64-7.67 (m, 1H, 7-H), 8.01-8.05 (m, 1H, 4-H); ^{13}C nmr (deuteriochloroform): δ 55.1, 74.3, 85.4, 110.5, 112.3, 113.9, 120.4, 124.6, 128.5, 128.6, 131.5, 132.1, 136.7, 145.9, 159.7.

Anal. Calcd. for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33. Found: C, 69.37; H, 5.11; N, 14.30.

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