The Synthesis of Pyrroles and Dihydropyrroles by 1,3-Dipolar Cyclisations of *N*-Arylmethylene[(benzotriazol-1-yl)arylmethyl]amines

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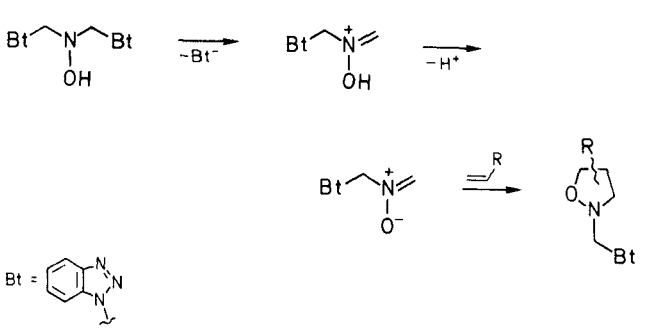
N-Arylmethylene[(benzotriazol-1-yl)arylmethyl]amines **1** are prepared by the reaction of arylaldehydes, benzotriazole, and ammonia in dry ethanol. Deprotonation of these imines with butyllithium yields *N*-lithiated azomethine ylides **2** which readily undergo 1,3-dipolar cycloaddition with a large range of dipolarophiles. The cyclisations are regiospecific and generally exhibit high stereoselectivity. Benzotriazolate is eliminated during the course of the reaction, and the method thereby provides a route to 2,5-diaryl substituted pyrroles, 3,4-dihydro-2*H*-pyrroles and *c*-ring fused 3,4-dihydro-2*H*-pyrroles.

1,3-Dipolar cycloadditions are of great interest to synthetic organic chemists, due to their ability to provide diastereoselective routes to a variety of 5-membered heterocyclic compounds. New methods to generate 1,3-dipoles, and the demonstration of the successful cycloaddition of such species is of consistent interest. We have been exploring the potential of *N*-substituted benzotriazoles as a source of reactive 1,3-dipolar species, and have previously reported the use of bis(benzotriazol-1-ylmethyl)hydroxylamine as a synthetic equivalent to the nitrone 1,3-dipole (Scheme **1**).[1] The generation of the nitrone 1,3-dipole in this system relies on the tendency of aminomethylbenzotriazoles to dissociate in solution by heterolytic cleavage.[2,3] We now report that *N*-arylmethylene[(benzotriazol-1-yl)arylmethyl]amines provide a convenient source of azomethine ylides which also undergo reaction with a wide range of dipolarophiles. Unlike the generation of the nitrone species, however, the formation of the azomethine ylide relies on the ability of benzotriazole to stabilise an adjacent negative charge.[4-6]



Scheme **1**

Imines which possess strongly electron-withdrawing α-substituents (-M effect) are known to undergo prototropic tautomerism to imine-azomethine ylides. Such ylides are formally 1,3-dipoles, and have been shown to undergo 1,3-dipolar cycloaddition with a variety of activated dipolarophiles to furnish substituted pyrrolidines and pyrroles.[7-14] Deprotonation of such imines by an external base would result in the formation of 2-azaallyl anions which may similarly undergo 1,3-anionic cycloaddition with suitable anionophiles to form 5-membered nitrogen heterocycles.[11,15] If the deprotonation of these imines is performed with a metallic base, coordination of the metal cation to the nitrogen of the 2-azaallyl anion may occur, resulting in the formation of *N*-metallated azomethine ylides.[16-21] Such deprotonation has been demonstrated,[22] and the *N*-metallated azomethine ylides often show differing stereoselectivity of cycloaddition compared to reactions which are performed under thermal equilibrium conditions without base.

The products of the cycloaddition of azomethine ylides with alkenic dipolarophiles are usually substituted pyrrolidines. There is a single report of the generation and cyclisation of azomethine ylides from imine precursors in which the activating group is also a leaving group. Thus, the reaction of *N*-(1-cyanoalkyl)imines[22] with alkenic dipolarophiles results in the formation of both substituted pyrrolidines and substituted dihydropyrroles; the latter compound being the result of elimination of cyanide during the course of the reaction. It is of significant interest to note that reverse stereoselectivities were often observed for the lithium diisopropylamide induced 1,3-dipolar cycloaddition of *N*-(1-cyanoalkyl)imines with electron-deficient alkenes, and the cycloaddition which occurs under the conditions of thermal prototropic deprotonation.[13,22-24] Furthermore, the metallated azomethine ylides generated from this system have proven reactive to dipolarophiles which are unreactive to the thermally produced 1,3-dipole.[22]

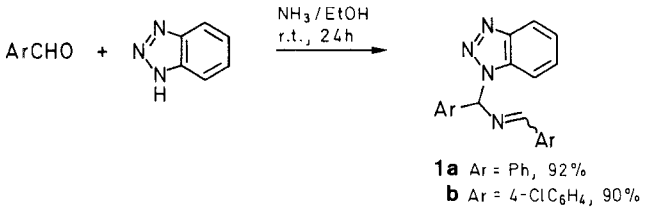
The condensation reaction of benzotriazole, amines, and aldehydes generally yields [1-(benzotriazol-1-yl)alkyl]amines.[2] The condensation reaction of benzotriazole, arylaldehydes, and ammonia, however, results in the formation of *N*-arylmethylene[(benzotriazol-1-yl)arylmethyl]amines in quantitative yield.[25] These compounds are analogous in structure to the *N*-(1-cyanoalkyl)imines and are considerably more stable. The benzotriazolyl substituent has been shown to stabilise an adjacent negative charge, although this effect is much smaller than that of a carboxylate or cyano substituent, as is shown by the failure of *N*-arylmethylene[(benzotriazol-1-yl)arylmethyl]amines **1** to undergo cycloaddition with dipolarophiles under thermal equilibrium conditions. Benzotriazolate is also an excellent leaving group when adjacent to an amino function; elimination of benzotriazolate from the cyclisation products is therefore expected to be facile.

The following report describes the reaction of *N*-benzylidene[α-(benzotriazol-1-yl)benzyl]amine (**1a**, Ar = Ph) with butyllithium and the subsequent cycloaddition with a variety of unsaturated dipolarophiles. Electron deficient alkenes undergo regiospecific cycloaddition, and generally exhibit a very high degree of stereoselectivity. In all cases, benzotriazolate is eliminated during the course of the reaction and substituted 3,4-dihydro-2,5-diphenyl-2*H*-pyrroles are iso-

lated. The reaction of an electron-deficient alkyne resulted in a high yield of the substituted 2,5-diphenylpyrrole. An example is given of the extension of the cycloaddition reaction to an imine formed from benzotriazole, ammonia and 4-chlorobenzaldehyde.

Stirring benzotriazole, benzaldehyde, and ammonia in dry ethanol or methanol at room temperature results in the quantitative precipitation of *N*-benzylidene[α-(benzotriazol-1-yl)benzyl]amine (**1a**, Ar = Ph) (Scheme **2**). Only one isomer is observed from NMR analysis, and on steric grounds this is presumed to be the *trans* isomer. The reaction of other arylaldehydes results in high yields of the analogous imines.

Treatment of **1a** (Ar = Ph) with one equivalent of butyllithium in tetrahydrofuran at −78 °C resulted in the immediate formation of a dark purple solution, presumably of the lithiated azomethine ylide **2a** (Ar = Ph) (Scheme **3**). Occasionally the colour of this solution was discharged on the addition of the alkene or alkyne, though this was not always the case. The reaction was allowed to continue for 5–6 hours at −78 °C before quenching. The reaction of the electron-deficient alkenes and alkynes resulted in 1,3-dipolar cyclisation, with subsequent elimination of benzotriazolate. No cycloadduct in which the benzotriazole group was retained was isolated from any reaction. The crude products from all cycloaddition reactions were analysed by NMR prior to chromatography, to determine possible stereomutation during the purification process. Estimated yields from ^{1}H-NMR spectra of all cycloadducts are in good agreement with isolated yields after purification (Tables 1 and 2).



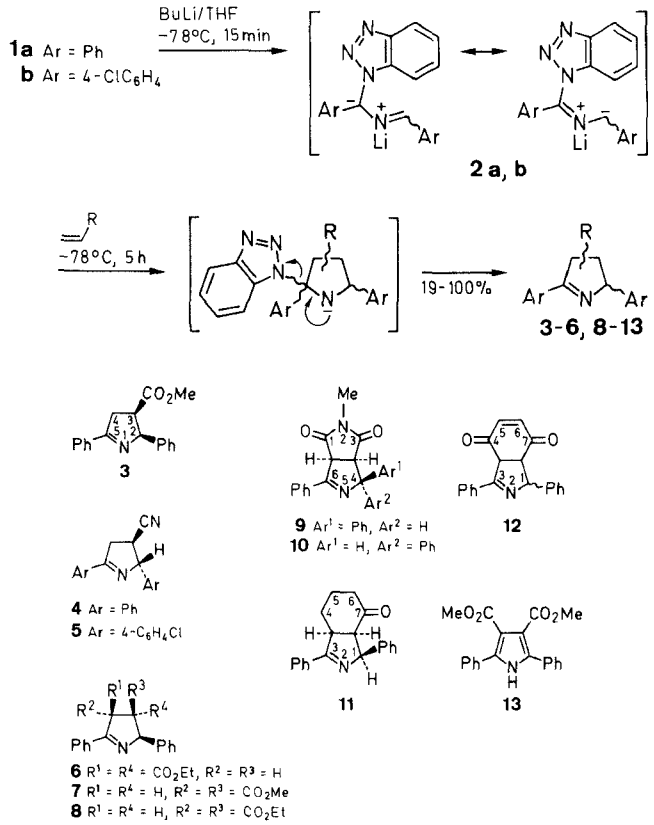
Scheme **2**

Where applicable the regiochemistry of these cycloaddition products was deduced by a combination of APT (attached proton tests), 2D-HETCOR (hetronuclear correlation spectroscopy), and proton decoupling experiments. Stereochemistry was determined predominantly by nuclear Overhauser enhancement (NOE) difference spectroscopy. The observation of moderate NOE enhancements for *trans* related vicinal protons is

Table 1. Cycloadducts **3–6** and **8–13** Prepared

Dipolarophile	Solvent for Chromatography	Cycloadduct	Yield (%)	mp (°C) (solvent)	Molecular Formula[a] or Lit. mp (°C)	IR (nujol or neat) ν (cm^{-1})	MS m/z (%)
methyl acrylate	$CHCl_3$/hexane (1:1)	**3**	95	112–113 °C (toluene/hexane)	104–105[13]	1728 (s, C=O), 1620 (s, C=N)	280 (M^+ + 1, 62), 279 (22), 220 (69), 219 (25), 193 (100), 165 (18), 115 (31)
acrylonitrile	Et_2O/hexane (1:3)	**4**	63	124.5–125.5 (EtOH)	$C_{17}H_{14}N_2$ (246.3)	2241 (w, C≡N), 1609 (w, C=N)	246 (M^+, 22), 194 (17), 193 (100), 165 (20), 90 (49), 89 (64)
		5	65	139–140 (EtOH)	$C_{17}H_{12}Cl_2N_2$ (315.2)	2241 (w, C≡N), 1613 (w, C=N)	315 (M^+, 7), 314 (20), 263 (35), 261 (54), 226 (41), 191 (12), 124 (15), 89 (100)
diethyl fumarate	$CHCl_3$/hexane (1:3) and then Et_2O/hexane (1:3)	**6**	95	oil	$C_{22}H_{23}NO_4$ (365.4)	1731 (s, C=O), 1620 (m, C=N)	365 (M^+, 23), 292 (41), 291 (78), 219 (52), 218 (48), 193 (100), 115 (36)
diethyl maleate	Et_2O/hexane (1:2)	**6/8**[b] (3:1)	47	oil	$C_{22}H_{23}NO_4$ (365.4)	1732 (s, C=O), 1626 (m, C=O)	–
N-methyl-maleimide	$CHCl_3$/hexane (1:4)	**9**	57	175–176 (EtOH)	178–179[13]	1777 (m, C=O), 1702 (s, C=O), 1615 (m, C=N)	305 (M^+ + 1, 21), 304 (M^+, 30), 219 (18), 193 (100), 165 (17), 115 (46), 90 (43), 89 (57)
		10	10	154–156 (toluene/hexane)	162–163[13]	1772 (m, C=O), 1700 (m, C=O), 1605 (m, C=N)	304 (M^+, 35), 193 (32), 126 (27), 113 (100)
2-cyclohexen-1-one	Et_2O/hexane (1:3)	**11**	65	134–135 (EtOH)	$C_{20}H_{19}NO$ (289.4)	1695 (s, C=O), 1620 (m, C=N)	290 (M^+ + 1, 26), 289 (M^+, 30), 261 (22), 233 (33), 232 (20), 193 (100), 165 (19)
Quinone	$CHCl_3$/hexane (1:4) and then Et_2O/hexane (1:1)	**12**	19	oil	$C_{20}H_{15}NO_2$ (301.4)	1667 (s, C=O)	301 (M^+, 12), 194 (18), 193 (100), 165 (9), 105 (12)
dimethyl butynedioate	$CHCl_3$/hexane (1:1)	**13**	~100	130–133 (toluene/hexane)	131–133[23]	3299 (s, NH), 1710 (s, C=O)	336 (M^+ + 1, 21), 335 (M^+, 100), 305 (18), 304 (93), 272 (20)

[a] All new compounds gave satisfactory microanalyses (C, H, N ±0.4) if solids, or HRMS data (C ±0.0076 amu) if oils.
[b] Inseparabe mixture of diastereoisomers.



Scheme 3

of note, and reflects the conformational flexibility of the 5-membered heterocyclic systems. Relevant data for all compounds are given in Tables 1 and 2, respectively. The results of the NOE investigations are reported as percentage differentials of the irradiated spectrum relative to the non-irradiated ^{1}H-NMR spectrum, and are given in Table 3. Stereochemical assignment of the cycloadducts is largely evident from the results of the NOE studies, and will be discussed only where necessary. In each case in which cycloaddition was observed, the reaction proceeded regiospecifically, and with a high degree of diastereoselectivity.

The cycloaddtion reactions of the monosubstituted alkenes methyl acrylate and acrylonitrile occured with identical regiospecificity, but opposite diastereoselectivity.

Thus, treatment of the solution of **2a** (Ar = Ph) with methyl acrylate resulted in a quantitative yield of a cycloadduct. NMR analysis indicated the product to consist of two diastereoisomers, one of which greatly predominated (95:5). Separation of the diastereoisomers could not be achieved chromatographically, however, only the major product was obtained from recrystallisation. The NOE studies of the product clearly indicated a *cis* relationship of the H-2 and H-3, and the structure was assigned as **3**. This compound has previously been reported as prepared by a different route.[13] The various data, particularly the ^{1}H and ^{13}C chemical shifts accord well with those of our sample. The stereochemistry of the minor product could not be assigned on the basis of the crude NMR spectra alone.

The reaction of **2a** (Ar = Ph) with acrylonitrile, however, resulted in the formation of only one cycloadduct in lower yield. In this case, much smaller NOE effects were observed between H-2 and H-3. To avoid ambiguity in the structural assignment, the reaction was repeated using the *N*-arylmethylene[benzotriazol-1-yl]amine derived from 4-chlorobenzaldehyde (**1b**, Ar = 4-ClC$_6$H$_4$). The electronic effect of the halide is highly unlikely to cause a change in reversal of stereoselectivity, whereas the *para* substitution would remove the possibility of a steric effect. Once again a single cycloadduct was obtained from the reaction, the alkyl region of which, on ^{1}H-NMR analysis, was identical to that of the product from the reaction of the *N*-phenylimine. Once again, small NOE effects are observed between H-2 and H-3, however, a NOE effect is also observed between the proton H-4 (δ = 3.36), which is *trans* to H-2, and H-3. This indicates that the products from both reactions with acrylonitrile to possess *trans* stereochemistry (i.e. **4** and **5**). In order to be quite sure of the stereochemistry and the position of the double bond, compound **5** was subjected to X-ray crystallography. The result, which confirmed the structure shown, will be reported elsewhere.

The reaction of the 1,2-disubstituted alkenes diethyl maleate and fumarate with **2a** (Ar = Ph) produced significantly different results. The *trans* diester gave an essentially quantitative yield of the 2,3,4-*trans* cycloadduct **6**; only traces of other isomers could be observed in the crude reaction product. The *cis* diester, however, furnished a mixture of two cycloadducts (3:1 ratio) in lower yield. The mixture could not be fully separated by column chromatography. The major cycloadduct was identified as the 2,3,4-*trans*-diastereoisomer **6**. The ^{1}H-NMR spectrum of the minor product shows the reasonances of the alkyl protons to have identical coupling constants and chemical shifts to those reported for **7**.[13] The minor diastereoisomer is therefore assigned the 2,3-*trans*-3,4-*cis*-structure **8**. It is unlikely that the initial 1,3-dipolar cycloaddition of **2a** (Ar = Ph) with diethyl maleate occurs in a manner which loses the stereointegrity of the alkene reagent (i.e. by an ionic 5-*endo*-*trigonal* ring closure[26]). The isolation of products in which H-3 and H-4 exhibit a *trans* relationship is presumably a result of C-3 epimerisation under the basic conditions of the reaction. Such epimerisation has previously been reported to explain the formation of **7** from the reaction of dimethyl maleate with *N*-benzylidene-α-cyanobenzylamine.[13]

The reaction of **2a** (Ar = Ph) with *N*-methylmaleimide resulted in the formation of two diastereoisomers of which one predominates. Again the isomer with a *cis* relationship between H-4 and H-3a is greatly preferred (*cis*-**9**: *trans*-**10**, 5.5:1). The cyclic unsymmetical alkene cyclohex-2-enone, however, undergoes regio- and diastereospecific reaction to yield **11**. The coupling patterns of H-3a and H-7a suggest the C-4 location of the carbonyl group. This structure has been confirmed by X-ray crystallography; the details will be published elsewhere.

The use of quinone as a dipolarophile is often inappropriate due to the initial cycloadduct product of such reac-

Table 2. ^{1}H- and ^{13}C-NMR Data of Cycloadducts **3–6** and **8–13**

Cyclo-adduct	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C-NMR ($CDCl_3$/TMS) δ
3	3.18 (s, 3H, CH_3), 3.20 (m, 1H, H-4), 3.66 (m, 1H, H-3'), 3.74 (m, 1H, H-3), 5.76 (dd, 1H, J = 9.0, 2.2, H-2), 7.16 (m, 2H$_{arom}$), 7.27 (m, 3H$_{arom}$), 7.48 (m, 3H$_{arom}$), 7.98 (m, 2H$_{arom}$)	38.00 (C-4), 48.06 (CH_3), 51.35 (C-3), 78.50 (C-2), 127.56, 127.62, 128.02, 128.58, 128.69, 131.04 (CH$_{arom}$), 133.70, 138.45 (C$_{arom}$), 172.43 (C-5), 173.11 (CO)
4	3.01 (m, 1H, H-3), 3.35 (ddd, 1H, J = 16.8, 8.7, 2.2, H-4), 3.60 (ddd, 1H, J = 16.8, 9.8, 1.9, H-3'), 5.53 (m, 1H, H-2), 7.24–7.53 (m, 8H$_{arom}$), 7.89 (dd, 2H$_{arom}$, J = 8.1, 1.5)	35.48 (C-3), 40.64 (C-4), 79.67 (C-2), 120.57, 126.14, 128.03, 128.08, 128.71, 128.91, 131.54, 132.70 (C$_{arom}$), 140.79 (C-5), 171.02 (CN)
5	2.98 (m, 1H, H-3), 3.36 (ddd, 1H, J = 16.9, 9.0, 2.3, H-4), 3.60 (ddd, 1H, J = 16.9, 9.8, 1.9, H-3'), 5.50 (d, 1H, J = 7.8, H-2), 7.25–7.47 (m, 6H$_{arom}$), 7.24 (m, 2H$_{arom}$)	35.60 (C-3), 40.67 (C-4), 78.97 (C-2), 120.09, 127.55, 129.11, 129.16, 129.22, 131.01, 134.16, 138.00 (C$_{arom}$), 139.10 (C-5), 170.36 (CN)
6	1.10 (t, 3H, J = 7.1, CH_3), 1.30 (t, 3H, J = 7.1, CH_3), 3.51 (t, 1H, J = 6.4, H-3), 4.09 (m, 2H, CH_2), 4.26 (m, 2H, CH_2), 4.70 (dd, 1H, J = 6.4, 1.6, H-4), 5.56 (dd, 1H, J = 6.4, 1.6, H-2), 7.40 (m, 8H$_{arom}$), 7.92 (dd, 2H$_{arom}$, J = 8.25, 1.9)	13.85 (CH_3), 14.22 (CH_3), 56.34 (C-4), 58.15 (C-3), 61.57, 61.62 (CH_2), 79.16 (C-2), 126.97, 127.59, 128.19, 128.48, 128.56, 131.06 (CH$_{arom}$), 132.86, 142.27 (C$_{arom}$), 168.50 (C-5), 170.83, 172.40 (CO)
8[a]	1.17 (t, 3H, J = 7.1, CH_3), 1.31 (t, 3H, J = 7.1, CH_3), 3.96 (dd, 1H, J = 9.0, 4.7, H-3), 4.10–4.30 (m, 4H, CH_2), 4.88 (dd, 1H, J = 4.7, 2.0, H-4), 5.88 (dd, 1H, J = 9.0, 2.0, H-2), 7.20–7.5 (m, 8H$_{arom}$), 8.01 (dd, 2H$_{arom}$, J = 3.3, 1.8)	13.97, 14.02 (CH_3), 53.75 (C-4), 57.43 (C-3), 61.25, 61.59 (CH_2), 78.41 (C-2), 127.76, 127.81, 128.10, 128.21, 128.44, 129.80 (CH$_{arom}$), 131.07, 131.16, (C$_{arom}$), 168.52 (C-5), 170.82, 169.03 (CO)
9	2.65 (s, 3H, CH_3), 4.00 (dd, 1H, J = 10.0, 8.8, H-3a), 4.67 (d, 1H, J = 8.8, H-6a), 5.92 (d, 1H, J = 10.0, H-4), 7.07 (m, 2H_{arom}), 7.30 (m, 3H_{arom}), 7.53 (m, 3H_{arom}), 8.26 (dd, 2H_{arom}, J = 7.35, 1.5)	24.81 (CH_3), 49.54, 56.79 (C-3a, 6a), 77.35 (C-4), 127.18, 128.28, 128.42, 128.55, 128.66, 131.73 (CH$_{arom}$), 131.88, 137.12 (C$_{arom}$), 167.39 (C-6), 173.12, 174.31 (CO)
10	3.00 (s, 3H, CH_3), 3.61 (dd, 1H, J = 8.5, 3.7, H-3a), 4.74 (dd, 1H, J = 8.5, 2.4, H-6a), 5.72 (t, 1H, J = 3.2, H-4), 7.26–7.52 (m, 8H$_{arom}$), 8.26 (m, 2H$_{arom}$)	25.27 (CH_3), 53.53, 56.34 (C-3a, 6a), 77.86 (C-4), 126.23, 127.76, 128.52, 128.92, 129.63, 131.71 (CH$_{arom}$), 131.76, 142.04 (C$_{arom}$), 166.49 (C-6), 173.02, 177.20 (CO)
11	0.87 (m, 1H), 1.42 (m, 1H), 1.62 (m, 1H), 1.81 (m, 1H), 2.10 (m, 2H), 3.6 (t, 1H, J = 9.6, H-7a), 3.76 (m, 1H, H-3a), 5.90 (d, 1H, J = 9.6, H-1), 7.14 (m, 2H$_{arom}$), 7.28 (m, 3H$_{arom}$), 7.51 (m, 3H$_{arom}$), 8.04 (m, 2H$_{arom}$)	24.07, 27.01, 41.12 (C-4, 5, 6), 49.35, 55.28 (C-3a, 7a), 76.35 (C-1), 127.32, 127.48, 128.32, 128.39, 128.80, 131.17, 132.74, 138.66 (C$_{arom}$), 176.42 (C-3), 211.53 (CO)
12	5.92 (dd, 1H, J = 10.2, 2.0, H-7a), 6.35 (m, 2H, H-1, 3a), 7.12, 7.25, 7.52, 8.08 (4m, 3H, 4H, 2H, 3H, 2H, resp., H$_{arom}$, H-5, 6)	78.53 (C-7a), 82.46 (C-1, 3a), 126.80, 128.35, 128.64, 128.69, 128.74, 128.98, 132.28, 136.62, 144.81, 146.72 (C$_{arom}$, C-6, and C-5), 163.82 (C-3), 184.93, 187.86 (CO)
14	3.69 (s, 6H, CH_3), 7.30 (m, 6H$_{arom}$), 7.49 (m, 4H$_{arom}$), 8.83 (br s, 1H, NH)	51.81 (CH_3), 114.05, 128.08, 128.52, 128.55, 130.72, 134.51 (C$_{arom}$), 165.78 (CO)

[a] Taken from NMR of a mixture of compounds **6** and **8**. Compound **8** was in too low a concentration to allow its separation.

Table 3. Results of ^{1}H-NOE Difference Spectroscopy Studies for Cycloadducts **3–6** and **9–12**

Cycloadduct	Irradiated Resonance, δ (Assignment)	Observed NOE Effect δ (%, Assignment)
3	3.70 (H-3/H-4)	7.88 (4.6, H$_{arom}$), 5.78 (6.6, H-2), 3.20 (14, H-3')
	5.76 (H-2)	7.17 (13.7, H$_{arom}$), 3.75 (9.4, H-3)
4	3.01 (H-3)	7.40 (5.8, H$_{arom}$), 5.53 (5.8, H-2), 3.60 (9.6, H-4)
	5.53 (H-2)	7.40 (10.7, H$_{arom}$), 3.01 (2.3, H-3)
5	2.98 (H-3)	7.32 (3.3, H$_{arom}$), 5.50 (4.0, H-2), 3.60 (7.0, H-4)
	3.36 (H-4)	7.84 (6.1, H$_{arom}$), 5.50 (3.0, H-2)
	3.60 (H-3')	7.84 (11.9, H$_{arom}$), 2.98 (17.2, H-3)
	5.50 (H-2)	7.32 (11.0, H$_{arom}$), 2.98 (2.3, H-3)
6	3.52 (H-3)	7.43 (8.8, H$_{arom}$), 5.57 (4.3, H-2), 4.72 (5.4, H-4)
	4.72 (H-4)	7.94 (16.7, H$_{arom}$), 5.57 (2.9, H-2), 3.52 (5.8, H-3)
	5.57 (H-2)	7.43 (16.5, H$_{arom}$), 4.72 (2.7, H-4), 3.52 (6.3, H-3)
9	4.00 (H-3a)	5.92 (15.6, H-4), 4.67 (14.8, H-6a)
	4.67 (H-6a)	8.26 (13.9, H$_{arom}$), 4.00 (13.0, H-3a)
	5.92 (H-4)	7.07 (18.7, H$_{arom}$), 4.00 (16.3, H-3a)
10	3.61 (H-3a)	4.74 (15.3, H-6a), 5.72 (5.7, H-4)
	4.74 (H-6a)	3.61 (13.2, H-3a), 8.26 (18.0, H$_{arom}$)
	5.72 (H-4)	3.61 (3.3, H-3a), 7.40 (10.6, H$_{arom}$)
11[a]	3.56 (H-7a)	5.90 (17.2, H-1)
	3.76 (H-3a)	8.04 (13.1, H$_{arom}$)
	5.90 (H-1)	3.56 (14.9, H-7a), 7.14 (13.4, H$_{arom}$)
12[b]	5.92 (H-7a)	6.36 (15.9, H-1/H-3a)
	6.36 (H-1/H-3a)	5.92 (6.5, H-7a), 7.08 (3.1, H$_{arom}$)

[a] Resonances of H-3a and H-7a are too close for unambiguous observation of NOE effects.
[b] Stereochemistry not assigned.

tions retaining a highly activated alkene bond which is capable of undergoing further reaction. A mixture of regioisomeric and diasterotopic cycloadducts, resulting from the reaction of one C=C bond, or both C=C bonds may be obtained. The reaction of quinone with one molar equivalent of **2a** (Ar = Ph) does indeed appear to result in a mixture of such cycloaddition products from which we have isolated a low yield of an unstable cycloadduct (which we tentatively assign as **12**) resulting from monoaddition. In this case, the superimposition of H-3a and H-7a resonances in the ^{1}H-NMR spectrum prevented the unambiguous assignment of stereochemistry by observation of NOE effects. No attempt was made to isolate further products.

No cycloadducts were isolated from the reaction of the electron-rich akene 3,4-dihydro-2*H*-pyran. Similarly, styrene, 2-vinylpyridine and 4-vinylpyridine also failed to undergo reaction.

Finally, the reaction of **2a** (Ar = Ph) with the electron deficient alkyne dimethyl butynedioate has been demonstrated. Thus, treatment of the solution of **2a** (Ar = Ph) with DMAD results in a quantitative yield of the pyrrole **13**. No reaction was observed between **2a** (Ar = Ph) and the terminal alkyne, phenylethyne.

In conclusion, *N*-arylmethylene[(benzotriazol-1-yl)arylmethyl]amines are deprotonated by butyllithium to yield lithiated azomethine ylides. These ylides are presumed to be the intermediates which undergo cycloaddition with a range of electron-deficient dipolarophiles in a regiospecific and diastereoselective manner to furnish 3,4-dihydro-2*H*-pyrroles. Electron-deficient alkynes undergo similar reactions to yield pyrroles.

Melting points were determined on a Fisher-Johns hot-stage melting point apparatus and are uncorrected. ^{1}H- 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 TMS as an internal standard. Nuclear Overhauser enhancement difference spectra were recorded on the same instrument; degassing of samples prior to NOE studies was found to be unnecessary. High resolution and electron impact source mass spectra were recorded on a Kratos AEI MS 30 with a Data General Nova data system. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR; spectra of solids were recorded as Nujol mulls, whereas oils were recorded neat. 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 (silica gel 60, mesh 240–400, Merck) which is used without further purification.

N-Benzylidene[α-(benzotriazol-1-yl)benzyl]amine (1a, Ar = Ph); Typical Procedure:

Benzaldehyde (0.85 g, 8 mmol) and benzotriazole (0.95 g, 8 mmol) are dissolved in a 2 molar anhydrous ethanolic ammonia solution (10 mL) and stirred at r.t. for 18 h. The precipitate is filtered, washed with anhydrous EtOH and dried under reduced pressure. Product **1** (Ar = Ph) is obtained as a white solid, which is used without further purification; yield: 1.2 g (92%).

*N-(4-Chlorobenzylidene)[α-(benzotriazol-1-yl)-4-chlorobenzyl]-amine (**1b**, Ar = 4-ClC$_6$H$_4$)*:

Precipitation does not occur and the product is obtained by removal of the solvent under reduced pressure. A yellow oil is obtained; yield is approx. 90% by NMR analysis, based on 4-chlorobenzaldehyde.

Reaction of *N*-Arylmethylene[(benzotriazol-1-yl)arylmethyl]amines with Dipolarophiles; Typical Procedure:

3a-cis-3a,4-cis-1,2,3,3a,4,6a-Hexahydro-2-methyl-1,3-dioxo-4,6-diphenylpyrrolo[3,4-c]pyrrole (**9**) *and 3a-cis-3a,4-trans-1,2,3,3a,4,6a-Hexahydro-2-methyl-1,3-dioxo-4,6-diphenylpyrrolo[3,4-c]pyrrole* (**10**): To a stirred solution of **1** (Ar = Ph) (0.2 g, 0.64 mmol) in THF (10 mL) is added a 2.5 molar solution of BuLi in hexanes (0.31 mL, 0.77 mmol) at −78 °C under N_2. *N*-Methylmaleimide (0.07 g, 0.64 mmol) dissolved in THF (5 mL) is then added, and the mixture stirred at −78 °C for 5 h, allowed to warm to r.t. and stirred overnight. After this period, the mixture is poured into 2M aq NH_4Cl (100 mL) and extracted with CH_2Cl_2. The organic extract is washed with H_2O (3 × 30 mL), and dried ($MgSO_4$). The solvent is removed under reduced pressure, and the crude oil separated into its components by flash chromatography using $CHCl_3$/hexane (1:4) as eluent. Compound **10** is eluted out first; yield: 20 mg (10.3%) followed by compound **9**; yield: 110 mg (57.0%) (Tables 1 and 2).

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