3-METHYL-1-PHENACYLBENZOTRIAZOLIUM YLIDE: CYCLOADDITIONS WITH ACETYLENIC ESTERS AND ALDEHYDE-MEDIATED DIMERIZATION

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Abstract - Stable 3-methyl-1-phenacylbenzotriazolium ylide (**2**) adds acetylene-carboxylic esters to form tricycles (**3**). Araldehydes react with two moles of **2** give poly-substituted 4,5-dihydrofurans (**5**). The pyrazoloquinoxaline structure of **3** was confirmed by X-ray analysis.

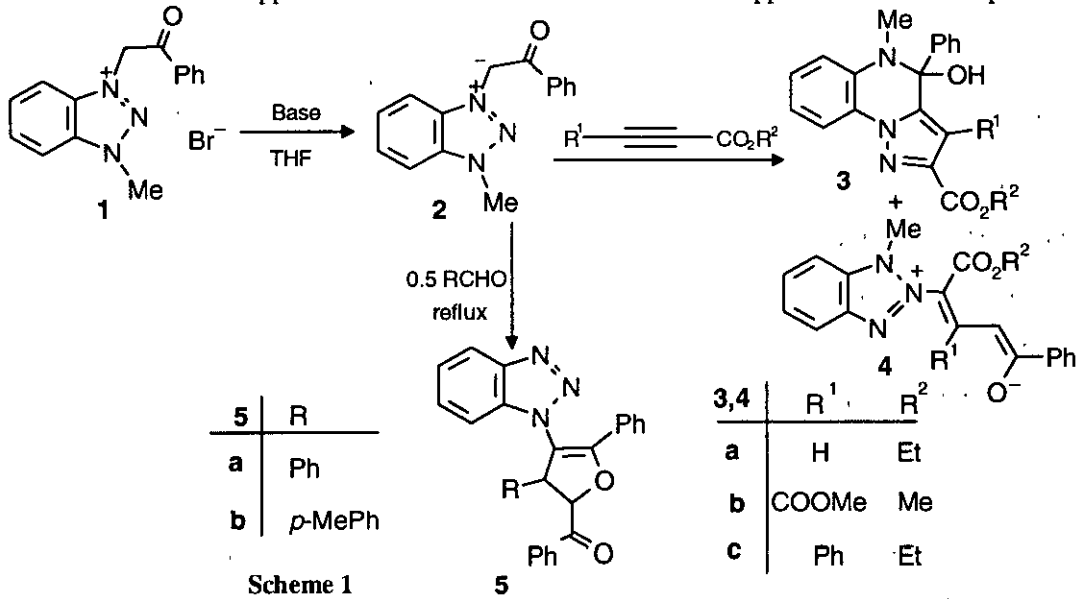
Cycloimmonium ylides are of great interest because of their reactivity, biological properties and applications.[1] Heterocyclic *N*-ylides such as pyridinium *N*-ylides have been intensively studied[2-3] particularly with regards to their 1,3-dipolar cycloadditions. Benzotriazolium salts and the corresponding ylides were reported long ago[4-8] as bactericides,[9-11] fungicides,[12] and dyes for acrylic fibers.[13-21] However, the reactions of benzotriazolium ylides are considered in very few papers: reactions with isocyanates or isothiocyanates[22] gave new betaines, and stable 3-dicyanomethyl-1-ethylbenzotriazolium ylide formed betaines of type (**4**) by 1,3-dipolar cycloadditions with a variety of acetylenic esters followed by ring opening.[23] Intramolecular [3+2] cycloaddition of 1-(4-pentynyl)benzotriazolium 3-dicyanomethylide led to a readily ring-opened cycloadduct.[24] Alvarez-Builla and coworkers reported that when benzotriazolium ylides were treated with dimethyl acetylenedicarboxylate (DMAD) as the dipolarophile, no identifiable products were isolated.[22]

Phosphorus ylides are extensively used in organic synthesis.[25] However, only a few reactions of the analogous *N*-ylides with aldehydes are reported,[1] and no accounts concerning the reactions of benzotriazolium ylides with aldehydes were located. We now report that benzotriazolium *N*-ylides react with acetylenic esters and with aldehydes, leading, upon rearrangement, to the formation of novel tricycles (**3**) and substituted dihydrofurans (**5**), respectively.

RESULTS AND DISCUSSION

3-Methyl-1-phenacylbenzotriazolium bromide (**1**) was prepared in 80% yield by refluxing 1-methyl- benzotriazole and α-bromoacetophenone in toluene for 5 hours. Compound (**1**) was conveniently converted to ylide (**2**) on treatment with either triethylamine or sodium carbonate in THF. Ylide (**2**) is stable in aqueous or ethanol solution and absorbs light in the visible region due to the extensive conjugation. When 3-methyl-1-phenacylbenzotriazolium ylide (**2**) was treated with acetylenic esters in THF, novel tricycles of type (**3**) (20-50 %) were obtained along with the known betaines of type (**4**) (Scheme 1). The reaction is regioselective, which is consistent with the theoretical prediction for the formation of **4** by the second order perturbational treatment.[26]

The structures of compounds (**3**) were supported by spectral and CHN analytical data. In the ^{1}H nmr spectra of compounds (**3**), the proton signal of the 3-methyl substituent is shifted to a higher field at 2.72 ppm, and the carbon signal to 31 ppm as compared with those of the corresponding salt (**1**) which appear at 4.72 ppm and 38.82 ppm, respectively. The chemical shifts indicate that the 3-methyl group is connected to an uncharged nitrogen atom. Similar compounds of type (**4**) were reported earlier,[23] and compound (**4a**) exhibits signals for the methyl group at 4.72 ppm in the ^{1}H nmr and at 37.6 ppm in the ^{13}C nmr spectrum. The CH= functionality of the enolate group in **4a** is observed at 4.25 ppm as a doublet in the ^{1}H nmr and at 90.22 ppm in the ^{13}C nmr spectrum.



5	R
a	Ph
b	*p*-MePh

3,4	R^1	R^2
a	H	Et
b	COOMe	Me
c	Ph	Et

Scheme 1

The structures of two of the rearranged tricycles (**3**) were determined by single crystal X-ray crystallography, namely the ethyl propiolate adduct (**3a**) and the methyl ether (**3b'**) resulting from recrystallization of the DMAD adduct (**3b**) from methanol. Figure 1 shows perspective views and atom labelling of these two structures. Bond

lengths and angles are given in Tables 1 and 2. The crystallography confirms the pyrazolo[1,5-*a*]quinoxaline framework for these two compounds and establishes the regiochemistry of the ethyl propiolate adduct (**3a**). Although this is a known heterocyclic ring system,[27] no X-ray structures have been previously reported. In both structures the pyrazolo[1,5-*a*]quinoxaline ring system is close to planar with C(4) and N(5) deviating slightly from the plane such that the central ring exists in a half chair conformation to which the phenyl substituent is attached in a pseudo-equatorial position. In both cases the phenyl ring is approximately orthogonal to the pyrazolo[1,5-*a*]-quinoxaline ring system (angles between the meanplanes: 81.1 and 83.9° for **3a** and **3b'** respectively). In both structures the C(2)- alkoxycarbonyl is approximately coplanar with the attached pyrazole ring (angles between the meanplanes: 7.2 and 0.1 ° for **3a** and **3b'** respectively), although in opposite geometrical relationships with respect to the C(2) - C(21) bond. For steric reasons the methoxycarbonyl substituent at C(3) in **3b'** is perpendicular (109.5°) to the plane of the pyrazole ring. The bond lengths and angles in the two structures are similar (Tables 1 and 2). However, the molecular packing differs, principally as a consequence of an intermolecular hydrogen bond in the case of **3a** wherein the OH group is hydrogen bonded to N(1) of an adjacent molecule with the following parameters: O(41) ··· N(1) = 3.059 Å; H(41) ··· N(1) = 2.22 Å; O(41)-H(41) ··· N(1) = 160°. In contrast there are no intermolecular contacts less than 3.29 Å between non-hydrogen atoms in the packing of **3b'**.

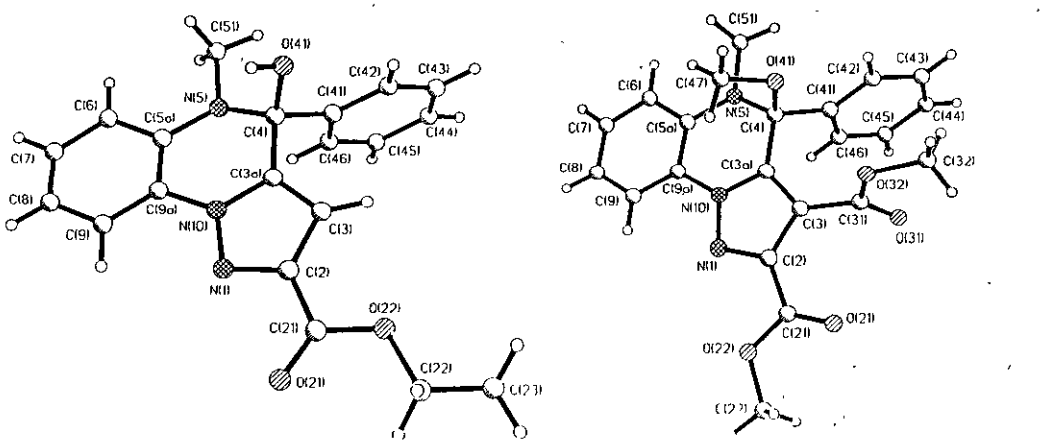
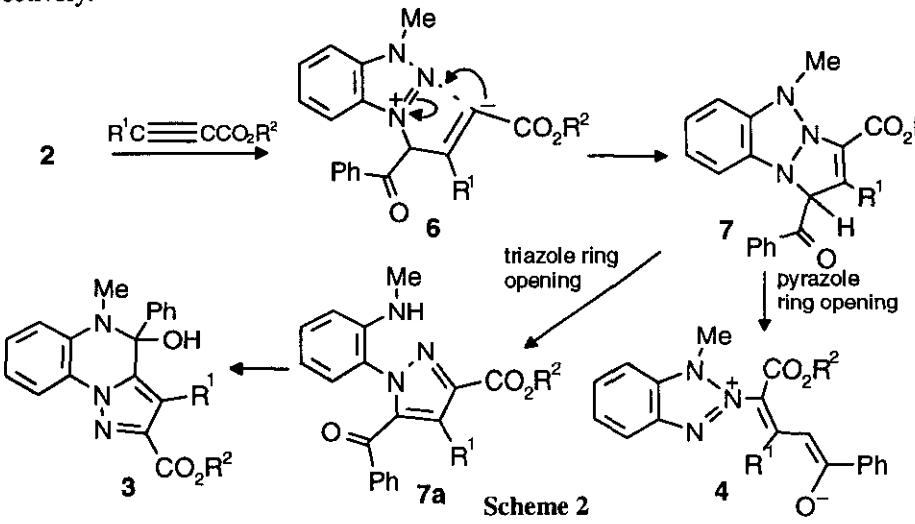


Figure 1. Perspective views and atom labelling of the crystal structures of **3a** and **3b'**

A mechanism for the formation compounds (**3**) and (**4**) from **2** *via* a rearrangement is proposed in Scheme 2. Cycloaddition of ylide (**2**) gives intermediate (**7**) which rearranges *via* two routes: a) the lone electron pair on nitrogen attacks the carbonyl group with subsequent N-N bond scission to give **3**; b) ring-opening of one five-membered ring as reported by Pardo[23] to afford **4.**

When 3-methyl-1-phenacylbenzotriazolium ylide (**2**) was refluxed with the appropriate aldehydes in THF for two

days 4,5-dihydrofurans (**5a**) and (**5b**) were obtained in yields of 22%-25% with simultaneous formation of 1-methylbenzotriazole (Scheme 1). Compounds (**5a,b**) were characterized by spectral data and CHN analyses. In the ^{1}H nmr spectrum of **5a**, two doublets at 5.08 ppm and 6.05 ppm are assigned to the 4- and 5-protons of the dihydrofuran ring. The two corresponding carbons were detected at 53.3 ppm and 87.5 ppm in the ^{13}C nmr spectrum, respectively.



Scheme 2

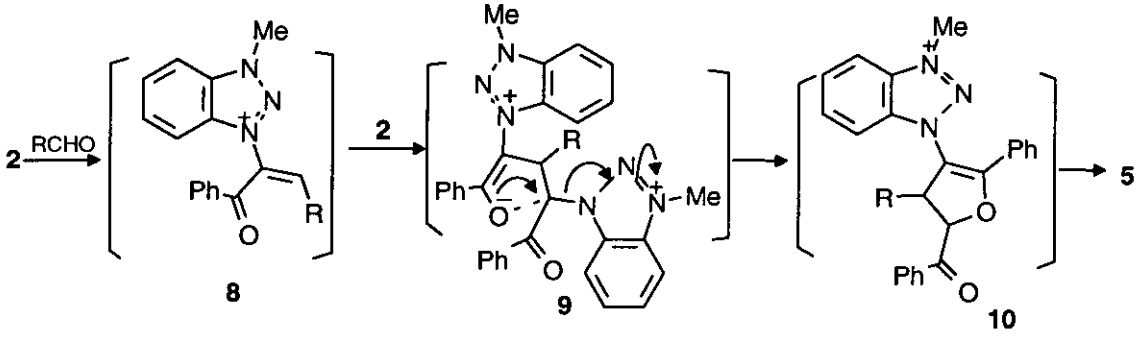
Table 1. Bond Lengths [Å] for **3a** and **3b'**

	3a	**3b'**		**3a**	**3b'**
N(1)-C(2)	1.336(2)	1.352(4)	N(1)-N(10)	1.346(2)	1.339(4)
C(2)-C(3)	1.397(2)	1.393(4)	C(2)-C(21)	1.470(3)	1.472(5)
C(3)-C(3A)	1.364(2)	1.380(4)	C(3)-C(31)		1 467(4)
C(3A)-N(10)	1.358(2)	1 358(4)	C(3A)-C(4)	1.499(2)	1.492(5)
C(4)-O(41)	1.422(2)	1.417(4)	C(4)-N(5)	1.453(2)	1 453(4)
C(4)-C(41)	1.527(2)	1.516(5)	N(5)-C(5A)	1.389(2)	1.385(4)
N(5)-C(51)	1.460(2)	1 458(4)	C(5A)-C(9A)	1.399(2)	1.386(4)
C(5A)-C(6)	1.392(3)	1.394(4)	C(6)-C(7)	1.380(3)	1.374(4)
C(7)-C(8)	1.371(3)	1.370(5)	C(8)-C(9)	1.376(3)	1.375(5)
C(9)-C(9A)	1.381(2)	1.366(4)	C(9A)-N(10)	1.408(2)	1.420(4)
C(21)-O(21)	1.204(2)	1.189(4)	C(21)-O(22)	1.332(2)	1.327(4)
O(22)-C(22)	1.453(2)	1.455(4)	C(22)-C(23)	1 446(3)	
C(31)-O(31)		1.202(4)	C(31)-O(32)		1 326(4)
O(32)-C(32)		1.437(4)	O(41)-C(47)		1.431(4)
C(41)-C-(46)	1.383(3)	1.373(5)	C(41)-C(42)	1 373(3)	1.375(4)
C(42)-C(43)	1.385(3)	1.397(5)	C(43)-C(44)	1.365(3)	1.365(5)
C(44)-C(45)	1.375(3)	1.369(5)	C(45)-C(46)	1.382(3)	1.371(5)

Table 2. Bond angles [°] for **3a** and **3b'**

	3a	**3b'**		**3a**	**3b'**
N(10)-N(1)-C(2)	103.7(1)	103.1(3)	N(1)-C(2)-C(3)	112.1(2)	112 2(3)
N(1)-C(2)-C(21)	118 0(2)	122.5(3)	C(3)-C(2)-C(21)	129.9(2)	125.3(3)
C(3A)-C(3)-C(2)	104.9(2)	105.0(3)	C(3A)-C(3)-C(31)		126.0(3)
C(2)-C(3)-C(31)		128 8(3)	N(10)-C(3A)-C(3)	106.5(2)	105.7(3)
N(10)-C(3A)-C(4)	121.9(2)	122.5(3)	C(3)-C(3A)-C(4)	131.4(2)	131 8(3)
O(41)-C(4)-N(5)	111.8(1)	111.6(3)	O(41)-C(4)-C(3A)	110.1(1)	110.2(3)
N(5)-C(4)-C(3A)	109.5(1)	110.3(3)	O(41)-C(4)-C(41)	106.8(1)	107.2(3)
N(5)-C(4)-C(41)	110.3(1)	109.6(3)	C(3A)-C(4)-C(41)	108.3(1)	107.9(3)
C(5A)-N(5)-C(4)	123.2(1)	123.4(3)	C(5A)-N(5)-C(51)	122.0(2)	118 9(3)
C(4)-N(5)-C(51)	115.0(1)	115.4(3)	N(5)-C(5A)-C(9A)	121.1(2)	122.2(3)
N(5)-C(5A)-C(6)	122.0(2)	120.9(3)	C(9A)-C(5A)-C(6)	116 8(2)	116.9(3)
C(7)-C(6)-C(5A)	120.6(2)	120 0(3)	C(8)-C(7)-C(6)	121.3(2)	121.8(3)
C(7)-C(8)-C(9)	119.7(2)	119.0(3)	C(9A)-C(9)-C(8)	119.1(2)	119 3(3)
C(9)-C(9A)-C(5A)	122.5(2)	122.9(3)	C(9)-C(9A)-N(10)	121.5(2)	121.1(3)
C(5A)-C(9A)-N(10)	116.1(2)	115.9(3)	N(1)-N(10)-C(3A)	112.8(1)	114.0(3)
N(1)-N(10)-C(9A)	123.4(1)	122.6(3)	C(3A)-N(10)-C(9A)	123.8(1)	123.2(3)
O(21)-C(21)-O(22)	124.8(2)	125.0(3)	O(21)-C(21)-C(2)	124.2(2)	123.0(3)
O(22)-C(21)-C(2)	111.0(2)	111 9(3)	C(21)-O(22)-C(22)	115.9(1)	114.4(3)
C(23)-C(22)-O(22)	108 8(2)		O(31)-C(31)-O(32)		123.8(3)
O(31)-C(31)-C(3)		124 3(3)	O(32)-C(31)-C(3)		111.8(3)
C(31)-O(32)-C(32)		115 3(3)	C(4)-O(41)-C(47)		114.6(3)
C(46)-C(41)-C(42)	119.2(2)	119.0(3)	C(46)-C(41)-C(4)	119.3(2)	118.6(3)
C(42)-C(41)-C(4)	121.4(2)	122 4(3)	C(41)-C(42)-C(43)	112.0(2)	119.9(4)
C(44)-C(43)-C(42)	110.7(2)	119.9(4)	C(43)-C(44)-C(45)	119.9(2)	120.2(3)
C(44)-C(45)-C(46)	119.6(2)	119 9(4)	C(45)-C(46)-C(41)	120.6(2)	121.1(3)

A mechanism for the conversion **2** to **5** is proposed in Scheme 3. First, ylide (**2**) reacts with an aldehyde to give α, β-unsaturated ketone (**8**) which undergoes Michael addition with another molecule of ylide (**2**) to give enolate intermediate (**9**). A subsequent intramolecular nucleophilic substitution forms compound (**10**) with the elimination of 1-methylbenzotriazole. Cation (**10**) finally undergoes thermal loss of one molecule of bromomethane to give compound (**5**).



Scheme 3

In conclusion, we have synthesized tricycles of type (**3**) for the first time from the reactions of benzotriazolium ylide with acetylenic esters. We have also discovered a novel reaction of benzotriazolium ylide with aldehydes producing 4,5-dihydrofuran derivatives (**5**).

EXPERIMENTAL

Melting points were determined on a Kofler hot stage apparatus and are reported without correction. ^{1}H Nmr: Varian VXR-300 nmr spectrometer (300 MHz) with TMS [δ(TMS) = 0.00] as the internal reference. ^{13}C Nmr: Varian VXR-300 Nmr spectrometer (75 MHz), referenced to the central line of $CDCl_3$ (δ = 77.0) or DMSO-d_6 (δ = 39.5). $CDCl_3$ or DMSO-d_6 was used as the solvent for both ^{1}H and ^{13}C nmr. High-resolution ms: Kratos/AE1-ms 30 mass spectrometer. Microanalyses: Carlo Erba 1106 elemental analysis. THF was distilled from sodium/benzophenone prior to use.

X-Ray Crystallography.

*Crystal Data for **3a**:* $C_{20}H_{19}N_3O_3$, Mr = 349.4, colorless prism from toluene/ethyl acetate, 0.55 × 0.49 × 0.18 mm; monoclinic, $P2_1/n$; a = 10.742(1), b = 12.628(1), c = 12.333(1)Ä, β = 92.57(1)°, V = 1671.5(3) Å^3; T = -133 °C, D_c = 1.39 g cm^{-3}; Z = 4, F(000) = 736, $2\theta_{max}$ = 50°; 240 parameters, wR2 = 0.097 for all 2938 data, R1 = 0.039 for 2036 data with $F_o > 4\sigma(F_o)$.

*Crystal Data for **3b'**:* $C_{22}H_{21}N_3O_5$, Mr = 407.4, colorless block from methanol, 0.30 × 0.24 × 0.15 mm; monoclinic, $P2_1/n$; a = 11.133(2), b = 16.523(3), c = 11.419(2)Å, β = 115.93(1) °, V = 1889.1(7) Å^3; T = -143 ° C, D_c = 1.43 g cm^{-3}; Z = 4, F(000) = 856, $2\theta_{max}$ = 48°; 275 parameters, wR2 = 0.099 for all 2794 data, R1 = 0.043 for 1406 data with $F_o > 4\sigma(F_o)$.

Data Collection, Structure Solution and Refinement: All measurements were made with a Nicolet P4s diffractometer using graphite monochromatized Mo Kα (λ = 0.71073Å) radiation. Throughout data collections (ω scans) the intensities of three standard reflections were monitored at regular intervals and this indicated no significant crystal decomposition. Intensities were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods using SHELXS-90,[28] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-92.[29] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier atoms. The functions minimized were Σ w (F_o2 - F_c2), with w = $[\sigma^2(F_o^2) + aP^2]^{-1}$ where P = $[\max(F_o^2) + 2F_c^2]/3$ and a = 0.0586 and 0.0456 for **3a** and **3b'** respectively. Final difference map features were all < 0.37 e $Å^{-3}$. Full tables of atom coodinates, thermal parameters, bond lengths, bond angles and structure factors are available from the author P. J. S. and have been deposited with the Cambridge Crystallographic Data Base.

Preparation of 3-Methyl-1-phenacylbenzotriazolium Bromide (Salt 1). A mixture of 1-methylbenzotriazole (13.3 g, 0.1 mol), and α-bromoacetophenone (19.9 g, 0.1 mol) was heated under reflux in toluene (200 ml) for 5 h. The mixture was cooled and the solid product collected by filtration and washed with ether (3 × 20 ml) to yield 26 g (80 %), mp 183-185 °C [lit., mp 148-150 °C].[22] ^{1}H Nmr (DMSO) δ: 4.72 (s, 3H), 7.16 (s, 2H), 7.69 (t, 2H, *J*=7.5 Hz), 7.82(t, 1H, *J*=7.5 Hz), 8.01-8.06 (m, 2H), 8.18 (d, 2H, *J*=7.5 Hz), 8.42-8.50 (m, 2H). ^{13}C Nmr (DMSO) δ: 190.0, 135.5, 135.0, 134.8, 133.4, 131.3, 130.8, 129.0, 128.7, 114.4, 114.2, 57.6, 38.8.

General Procedure for the Preparation of 3 and 4 from Benzotriazolium Salt (1) and Acetylenic Esters.
A mixture of 3-methyl-1-phenacylbenzotriazolium bromide (2 mmol), acetylenic ester (4 mmol) and triethylamine (2 ml) in THF (20 ml) was vigorously stirred at room temperature for two days. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel).

*Reaction of salt (**1**) with ethyl propiolate, formation of pyrazoloquinoxaline (**3a**) and betaine (**4a**).* **3a** was isolated in 52% yield, mp 194-196 °C. ^{1}H Nmr ($CDCl_3$) δ: 1.25 (t, 3H, *J*=7.0 Hz), 2.71 (s, 3H), 4.24 (q, 2H, *J*=7.0 Hz), 6.20 (s, 1H), 6.79 (s, 1H), 6.84-6.90 (m, 2H), 7.15-7.35 (m, 4H), 7.45-7.55 (m, 2H), 8.06 (d, 1H, *J*=7.8 Hz). ^{13}C Nmr ($CDCl_3$) δ: 161.2, 142.8, 142.2, 141.0, 135.1, 127.4, 127.3, 126.9, 125.9, 122.7, 117.3, 114.9, 112.4, 106.2, 83.6, 60.0, 30.8, 13.5. Anal. Calcd for $C_{20}H_{19}N_3O_3$: C, 65.74; H, 5.24; N, 11.50. Found C, 65.41; H, 5.23; N, 11.44. **4a** was formed in 30% yield, mp 162 °C (decomp.). ^{1}H Nmr (DMSO-d_6) δ: 1.05 (t, 3H, *J*=7.0 Hz), 3.88 (q, 2H, *J*=7.0 Hz), 4.27 (d, 1H, *J*=11.5 Hz), 4.65 (s, 3H), 7.40-7.50 (m, 3H), 7.53-7.62 (m, 2H), 7.80-7.95 (m, 4H), 8.28-8.34 (m, 1H). ^{13}C Nmr (DMSO-d_6) δ: 179.6, 167.9, 142.4, 141.4, 135.4, 135.0, 130.3, 130.1, 128.6, 127.8, 114.3, 113.8, 105.1, 90.3, 90.2, 57.7, 37.6, 14.3.

*Reaction of salt (**1**) with dimethyl acetylenedicarboxylate, formation of pyrazoloquinoxaline (**3b**).* **3b** was isolated in 25% yield, mp 175-177 °C. ^{1}H Nmr ($CDCl_3$) δ: 2.81 (s, 3H), 3.62 (s, 3H), 3.95 (s, 3H), 6.08 (s, 1H), 6.80 (d, 1H, *J*=8.0 Hz), 6.95 (t, 1H, *J*=8.0 Hz), 7.24-7.35 (m, 6H), 8.11 (d, 2H, *J*=8.0 Hz). ^{13}C Nmr ($CDCl_3$) δ: 165.2, 141.7, 141.6, 136.2, 135.2, 134.9, 128.6, 128.1, 126.6, 125.6, 118.1, 116.6, 112.4, 111.4, 85.1, 52.5, 52.4, 30.2. Anal. Calcd for $C_{20}H_{19}N_3O_5$: C, 66.83; H, 5.07; N, 11.13. Found C, 66.58; H, 5.05; N, 11.05.

*Reaction of salt (**1**) with ethyl phenylpropiolate, formation of pyrazoloquinoxaline (**3c**).* **3c** was isolated in 20% yield, mp 197-199 °C. ^{1}H Nmr ($CDCl_3$) δ: 1.05 (t, 3H, *J*=7.0 Hz), 2.71 (s, 3H), 3.15 (br s, 1H), 4.14(q, 2H, *J*=7.0 Hz), 6.75 (d, 2H, *J*=8.0 Hz), 6.85 (d, 1H, *J*=8.0 Hz), 6.95-7.12 (m, 9H), 7.22-7.30 (m, 1H), 8.24 (d, 1H, *J*=8.0 Hz). ^{13}C Nmr ($CDCl_3$) δ: 167.7, 145.6, 141.1, 135.2, 131.2, 130.3, 130.2. 130.1, 127.5, 127.3, 127.0, 126.8, 126.7, 126.5, 118.7, 116.4, 112.9, 112.8, 85.4, 60.7, 31.1, 13.8. Anal. Calcd for $C_{26}H_{23}N_3O_3$: C, 73.39; H, 5.45; N, 9.88. Found C, 73.41; H, 5.42; N, 9.88.

General Procedure for the Preparation of Compounds (5) from Benzotriazolium Salt (1) and Aldehydes.
A mixture of 3-methyl-1-phenacylbenzotriazolium bromide (2 mmol), aldehyde (2 mmol) and triethylamine (2 ml) in THF (20 ml) was stirred under reflux for two days. The solvent was removed under vacunm and the residue was purified by column chromatography (silica gel).

*Reaction of salt (**1**) with benzaldehyde, formation of 2,4-diphenyl-3-(benzotriazol-1-yl)-5-benzoyl-4,5-dihydrofuran (**5a**).* **5a** was isolated in 25% yield, mp 201-203 °C. ^{1}H Nmr ($CDCl_3$) δ: 5.08 (d, 1H, *J*=5.1 Hz), 6.05 (d, 1H, *J*=5.1 Hz), 7.14-7.35 (m, 11H), 7.37-7.42 (m, 2H), 7.53 (t, 2H, *J*=7.3 Hz), 7.64 (t, 1H, *J*=7.3 Hz), 7.98 (d, 1H, *J*=7.3 Hz), 8.06 (d, 2H, *J*=7.3 Hz). ^{13}C Nmr ($CDCl_3$) δ: 193.2, 152.1, 145.4, 139.3, 134.1, 133.7, 133.5, 130.3, 129.2, 129.1, 128.9, 128.4, 128.1, 128.0, 127.9, 127.5, 126.9, 124.0, 119.9, 111.1, 110.1, 87.5, 53.3, Anal. Calcd for $C_{29}H_{21}N_3O_2$: C, 78.53; H, 4.78; N, 9.48. Found C, 78.11; H, 4.74; N, 9.29.

*Reaction of salt (**1**) with p-methylbenzaldehyde, formation of 2-phenyl-3-(benzotriazol-1-yl)-4-(p-methylphenyl)-5-benzoyl-4,5-dihydrofuran (**5b**).* **5b** was isolated in 22% yield, mp 121-123 °C. ^{1}H Nmr ($CDCl_3$) δ: 2.25 (s, 3H), 5.03 (d, 1H, *J*=5.1 Hz), 6.03 (d, 1H, *J*=5.1 Hz), 7.10-7.30 (m, 12H), 7.51 (t, 2H, *J*=7.3 Hz), 7.63 (t, 1H, *J*=7.3 Hz), 7.98 (d, 1H, *J*=7.3 Hz), 8.06 (d, 2H, *J*=7.3 Hz). ^{13}C Nmr ($CDCl_3$) δ: 193.3, 151.9, 145.4, 137.8, 136.2, 134.0, 133.7, 133.5, 130.2, 129.8, 129.7, 129.2, 128.9, 128.4, 127.8, 127.6, 126.9, 124.0, 120.0, 111.2, 110.2, 85.6, 53.0, 21.0. Anal. Calcd for $C_{30}H_{23}N_3O_2$: C, 78.76; H, 5.07; N, 9.18. Found C, 78.96; H, 5.13; N, 9.19.

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