1-(Azidomethyl)benzotriazole and -5-phenyl-1,2,3,4-tetrazole as 1,3-Dipolar Cycloaddition Components

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Received August 11, 1995

1-(Azidomethyl)benzotriazole reacts with alkynes to give mixtures of isomeric 1,2,3-triazoles, whereas the interactions of 1-(azidomethyl)benzotriazole and -5-phenyl-1,2,3,4-tetrazole with alkenes proceed regioselectively to form 1,2,3-triazolines and/or aziridines and enamines in good yields. Diheterocyclo-substituted methanes thus obtained were investigated with respect to thermolysis, α-lithiation, and reactions with Grignard reagents.

J. Heterocyclic Chem., **33**, 335 (1996).

Introduction.

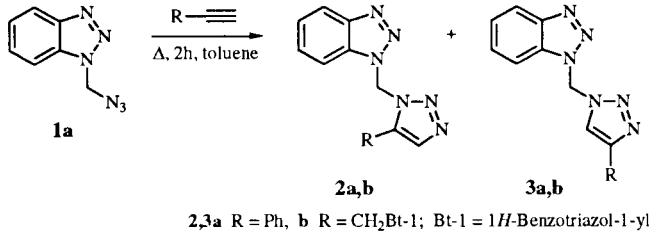
1,3-Dipolar cycloaddition reactions of alkyl and aryl azides are well investigated [1]: their reactions with alkynes give mixtures of isomeric 1,2,3-triazoles, whereas those with alkenes proceed regioselectively to form 1,2,3-triazolines. In some cases, aziridines or enamines are produced by 1,2,3-triazoline ring transformation.

Cycloadditions to azido groups attached to carbon atoms of a heterocycle directly or through a methylene group(s) are of recent interest. 2-Azidobenzo[*b*]thiophenes underwent thermolysis in the presence of alkenes to give aziridines and/or 4-cyanoisochromans [2,3]. In reactions with alkyl acrylates, 6-azidobenzothiazoles formed 1,2,3-triazolines, which were cleaved in the presence of bases to give diazopropanoic acid esters [4]. 2- and 4-Azidopyrimidines reacted with acetylacetone to yield pyrimidinyl-substituted acetyltriazoles [5]. In additions to various carbon-carbon triple bond systems, 2-azidothiazoles readily formed the corresponding triazoles, which on photolysis yielded imidazo[4,1-*b*]thiazoles [6]. HIV activity tests were reported for 2',3'-dideoxy-3'-(triazol-1-yl)uridenes obtained from 3-azidotetrahydrofuran derivatives by a cycloaddition reaction [7]. 2-Azidomethyl-3-arylquinazolines [8], 2-azidomethyloxiranes [9] and 2-(4-pyridyl)ethyl azide [10], smoothly yielded the corresponding 1,2,3-triazoles in reactions with alkynes. Syntheses of tris-triazoles by cycloadditions of alkynes to 4,5-di(azidomethyl)-1,2,3-triazoles were reported [11]. In spite of these and numerous other investigations in azide chemistry, we found no literature data on cycloaddition reactions of any azidomethyl group attached to a heteroatom of a heteroaromatic ring. 1-(Azidomethyl)benzotriazole (**1a**), which is an example of such a type of azide, was recently synthesized in our laboratory by reaction of 1-(chloromethyl)benzotriazole with sodium azide [12]. Using the same approach, 1-(azidomethyl)-5-phenyl-1,2,3,4-tetrazole (**1b**) was readily obtained. We now report an investigation of the cycloaddition reactions of 1-(azidomethyl)heterocycles **1a,b** with alkynes and alkenes.

Results and Discussion.

1-(Azidomethyl)benzotriazole (**1a**) reacted with phenylacetylene, and with propargylbenzotriazole, to give mixtures of the 1,2,3-triazoles **2a** and **3a**, and **2b** and **3b**, respectively (Scheme 1). Isomers **2a** and **3a** were isolated by column chromatography in 60% and 40% yields, and **2b** and **3b** were separated by fractional crystallization in 27% and 45% yields, respectively. The structures of triazoles **2a,b** and **3a,b** were confirmed by NOE nmr experiments; the formation of two isomers in each case is in agreement with the previously described additions of alkyl- and aryl-azides to acetylenes [1]. In contrast to the benzotriazole derivatives of type Bt-C-X (X = OR, NR_2, *etc.*), which are activated towards electrophilic substitution in the Grignard reaction [13], triazoles 2 and 3 were unchanged after refluxing with PhMgX or $PhCH_2ZnX$ in toluene for several days.

Scheme 1



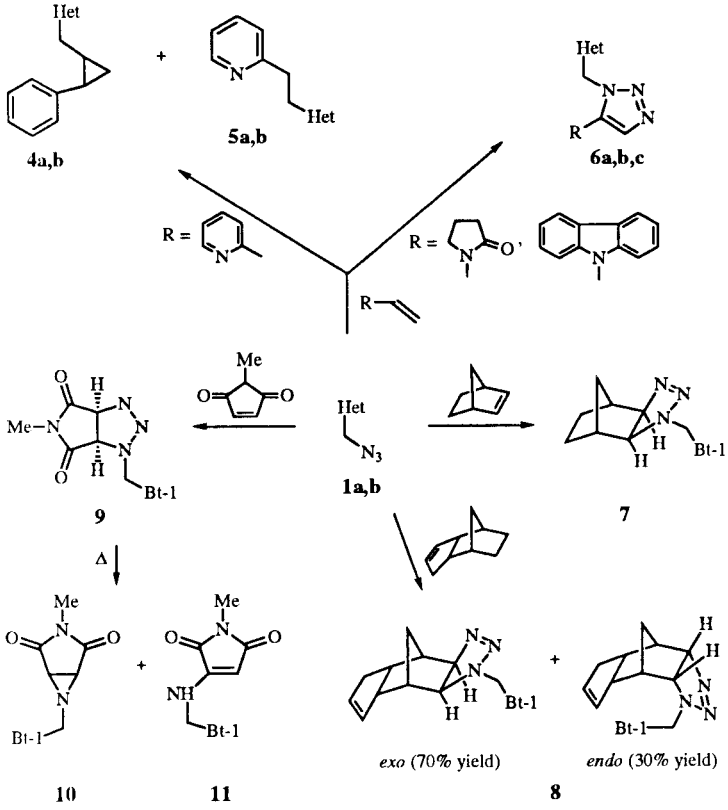
1a **2a,b** **3a,b**

2,3a R = Ph, **b** R = CH_2Bt-1; Bt-1 = 1*H*-Benzotriazol-1-yl

The products from cycloadditions of alkenes to the azido group in **1a,b** depend upon the alkene structure (Scheme 2). Thus, azides **1a,b** react with 2-vinylpyridine in toluene for 48 hours to give the respective aziridines **4a** (60%) and **4b** (40%) together with the Michael addition products **5a** (40%) and **5b** (30%). The formation of 1-(benzotriazol-2-yl)-2-R-substituted ethanes of type **5a** occurred also in reactions of electron-deficient alkenes, with 1-(*N*-morpholino)- or 1-(*N*-morpholino)-1-phenylmethylbenzotriazole [14], and may be considered as a formal addition of benzotriazole to the double bond of an

alkene. The structures of aziridines **4a,b**, which result from thermal ring fission of the intermediate 1,2,3-triazolines similarly to previous examples [15], were confirmed by the chemical shifts and coupling constants of the protons in the three membered ring (*cf.* experimental section and [16]).

Scheme 2



1a Het = Bt-1, **b** Het = Tetr; **4a** Het = Bt-1, R = pyrid-2-yl; **b** Het = Tetr, R = pyrid-2-yl; **5a** Het = Bt-2, **b** Het = Tetr; **6a** R = pyrrolid-2-on-1-yl, **b** R = carbazol-1-yl, **c** Het = Tetr, R = pyrrolid-2-on-1-yl; Bt-1 = 1*H*-Benzotriazol-1-yl; Tetr = 5-Phenyl-1,2,3,4-tetrazol-1-yl

1,2,3-Triazolines **6a,b, 7** and **8** were isolated from reactions of **1a** with the corresponding electron-rich alkenes in 65-85% yields. The reaction of **1a** with norbornene led exclusively to the *exo* isomer of triazoline **7**. Earlier, we described the formation of an *exo* aziridine isomer from the reaction of norbornene with 2-(4-pyridyl)ethyl azide [10], where the intermediate triazoline ring formed is evidently less thermally stable than that of **7**. Structure **7** was confirmed by the strongly shielded *anti* H-bridge signal in the ^{1}H nmr spectrum (δ 0.91), which is typical for the *exo* isomers of norbornene adducts [1]. Dicyclopentadiene reacted with azide **1a** only at the norbornene double bond in agreement with previously reported analogous additions, which formed *exo* adducts only [15]. However, triazoline **8** was isolated as an inseparable mixture of the *exo* and *endo* isomers in a 2.5:1 ratio. The *endo* isomer may be stabilized in this case by an electronic interaction of the benzotriazolyl substituent with the alkene fragment in **8**. Triazolines **6a,b, 7** and **8** were stable on thermolysis up to 200°, and the formation of aziridines or the ring opened products was not observed. A similar surprising thermal stability was reported for the trimethylsilyl-substituted triazoline adducts of norbornene or dicyclopentadiene with trimethylsilyl azide [17].

Azide **1a** reacted with *N*-maleimide in refluxing toluene for 3 hours to give exclusively triazoline **9**. However, when the reaction was carried out for 24 hours, a mixture of triazoline **9** and the expected products of its ring transformation, aziridine **10** and enamine **11**, was isolated in a 4:2:1 ratio. Refluxing triazoline **9** in toluene for 24 hours yielded a mixture of **10** and **11** in a 4:1 ratio. Thus, the thermal stability of the 1,2,3-triazolines obtained is determined by the substituents at the heterocyclic ring: the higher the electron-withdrawing effect of the substituent, the more readily elimination of nitrogen occurs with subsequent formation of aziridines and/or enamines.

We expected ready lithiation at the 1-methylene group in triazolines of type **7** or **9**, and in aziridines of type **4**, and that the anions formed should undergo electrophilic substitution similar to the examples described for 1-methoxymethylbenzotriazole [13]. However, treatment of adducts **7, 9** and **4a** with *n*-butyllithium or lithium diisopropylamide at -78° in tetrahydrofuran solution, followed by addition of alkyl iodides or benzyl bromide, led to complete destruction of the starting material, and only benzotriazole was isolated in *ca* 90% yield. Decomposition was also observed in reactions of the same adducts with phenylmagnesium or methylmagnesium iodide in refluxing toluene. Thus, the triazoline ring in **7** decomposes under conditions of both electrophilic and nucleophilic substitution.

Conclusion.

Cycloaddition reactions of 1-(azidomethyl)benzotriazole with alkynes gave mixtures of the expected isomeric (benzotriazol-1-yl)methyl-substituted 1,2,3-triazoles, but attempts to replace the benzotriazole group in Grignard reactions failed. The use of alkenes as dienophiles in reactions of 1-(azidomethyl)-benzotriazole or -5-phenyl-1,2,3,4-tetrazole gave triazolines or aziridines depending upon the structure of the azide and the dienophile used.

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The ^{1}H and ^{13}C nmr spectra were recorded on a Gemini 300 spectrometer (300 and 75 MHz respectively) using deuteriochloroform as solvent. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. Commercially available reagent grade solvents were dried over sodium-benzophenone. Flash column

chromatography was run over EM Science silica gel (230-400 mesh). 1-(Azidomethyl)benzotriazole (**1a**) was prepared according to the previously described method [12].

1-Azidomethyl-5-phenyl-1,2,3,4-tetrazole (**1b**).

A mixture of 1-chloromethyl-5-phenyl-1,2,3,4-tetrazole (1.0 g, 5 mmoles) and sodium azide (0.5 g, 7.6 mmoles) in dimethyl sulfoxide (10 ml) was stirred at room temperature for 12 hours. The mixture was poured into water (40 ml), and a colorless precipitate was filtered off, dried and recrystallized from isopropyl alcohol-hexane (1:1) to give **1b** (68%), mp 84-86°; ^{1}H nmr: δ 8.17-8.22 (m, 2H), 7.48-7.53 (m, 3H), 5.68 (s, 2H); ^{13}C nmr: δ 166.1, 130.8, 129.0, 127.0, 126.7, 65.3.

Anal. Calcd. for $C_8H_7N_7$: C, 47.76; H, 3.51; N, 48.73. Found: C, 47.87; H, 3.46; N, 49.01.

Reaction of 1-(Azidomethyl)benzotriazole (**1a**) with Phenylacetylene.

A mixture of **1a** (0.52 g, 3 mmoles) and phenylacetylene (0.8 g, 3.2 mmoles) in toluene (3 ml) was refluxed for 2 hours. The solution was cooled, and hexane (10 ml) was added to form a colorless oil. The mixture was refluxed until the oil crystallized (about 3 minutes). The product was filtered off, dried and purified by flash chromatography (chloroform) to give separation of **2a** (60%) and **3a** (40%).

1-(Benzotriazol- 1-ylmethyl)-5-phenyl-1,2,3-triazole (**2a**).

This compound was obtained as colorless plates (isopropyl alcohol), mp 165-168°; ^{1}H nmr: δ 8.06 (d, 1H, J = 8.4 Hz), 7.98 (d, 1H, J = 8.4 Hz), 7.71 (s, 1H), 7.53-7.60 (m, 6H), 7.42 (dd, 1H, J_1 = 7.5 Hz, J_2 = 7.7 Hz), 7.06 (s, 2H); ^{13}C nmr: δ 146.2, 139.0, 133.4, 132.7, 130.2, 129.3, 128.7, 125.3, 124.8, 120.0, 110.7, 57.7.

Anal. Calcd. for $C_{15}H_{12}N_6$: C, 65.21; H, 4.38; N, 30.42. Found: C, 64.86; H, 4.34; N, 30.74.

1-(Benzotriazol-1-ylmethyl)-4-phenyl-1,2,3-triazole (**3a**).

This compound was obtained as colorless plates (isopropyl alcohol), mp 171-173°; ^{1}H nmr: δ 8.08 (d, 1H, J = 8.3 Hz), 8.03 (s, 1H), 7.87 (d, 1H, J = 8.4 Hz), 7.75-7.79 (m, 2H), 7.53-7.60 (m, 1H), 7.32-7.46 (m, 4H), 7.17 (s, 2H); ^{13}C nmr: δ 146.4, 146.2, 132.3, 129.6, 128.9, 128.8, 128.6, 125.8, 125.0, 120.2, 119.3, 109.7, 59.4.

Anal. Calcd. for $C_{15}H_{12}N_6$: C, 65.21; H, 4.38; N, 30.42. Found: C, 64.99; H, 4.35; N, 30.82.

Reaction of 1-(Azidomethyl)benzotriazole (**1a**) with 1-Propargylbenzotriazole.

A mixture of **1a** (0.16 g, 1 mmole) and 1-propargylbenzotriazole (0.20 g, 1.1 mmoles) in toluene (3 ml) was refluxed for 2 hours. The solution was cooled, and **3b** (45%) was filtered off. The filtrate was evaporated *in vacuo* to give **2b** (27%).

1,5-Di(benzotriazol-1-ylmethyl)-1,2,3-triazole (**2b**).

This compound was obtained as colorless plates (isopropyl alcohol), mp 138-140°; ^{1}H nmr: δ 8.04-8.09 (m, 2H), 7.92 (d, 1H, J = 8.4 Hz), 7.66 (s, 1H), 7.41-7.62 (m, 5H), 7.37 (s, 2H), 6.21 (s, 2H); ^{13}C nmr: δ 146.1, 145.9, 135.2, 132.5, 132.3, 131.6, 129.1, 128.4, 125.1, 124.5, 120.4, 120.2, 109.9, 108.8, 57.6, 39.6.

Anal. Calcd. for $C_{16}H_{13}N_9$: C, 57.98; H, 3.96; N, 38.06. Found: C, 57.86; H, 3.94; N, 38.39.

1,4-Di(benzotriazol-1-ylmethyl)- 1,2,3-triazole (**3b**).

This compound was obtained as colorless plates (isopropyl alcohol), mp 208-211° (isopropyl alcohol); ^{1}H nmr: δ 8.02-8.08 (m, 2H), 7.85 (s, 1H), 7.79 (d, 1H, J = 8.4 Hz), 7.67 (d, 1H, J = 8.3 Hz), 7.54-7.59 (m, 1H), 7.32-7.48 (m, 3H), 7.06 (s, 2H), 5.91 (s, 2H); ^{13}C nmr: δ 143.6, 129.0, 127.8, 125.1, 124.2, 123.0, 120.4, 120.1, 113.4, 109.7, 109.5, 59.2, 43.3.

Anal. Calcd. for $C_{16}H_{13}N_9$: C, 57.98; H, 3.96; N, 38.06. Found: C, 57.81; H, 3.94; N, 38.40.

Reaction of Azides **1a,b** with 2-Vinylpyridine.

2-Vinylpyridine (0.78 g, 7.5 mmoles) was added to the appropriate azide (5.7 mmoles) in toluene (50 ml) and the mixture was refluxed for 48 hours. The reaction was monitored by tlc until the starting materials had been consumed. The solvent was evaporated *in vacuo* to give an oily crude mixture of **4a** and **5a**, and **4b** and **5b** which was separated by flash chromatography (benzene-acetone, 7:3) in 60% and 40%, and 30% and 20% yields, respectively.

1-(Benzotriazol-1-ylmethyl)-2-(pyrid-2-yl)aziridine (**4a**).

This compound was obtained as light yellow needles (ethyl alcohol) mp 98-100°; ^{1}H nmr: δ 8.40 (d, 1H, J = 4.2 Hz, α-pyridyl), 8.04 (d, 1H, J = 8.4 Hz, 7-H, Bt-1), 7.54 (d, 1H, J = 8.3 Hz, 5-H, Bt-1), 7.47-7.58 (m, 2H), 7.32-7.38 (m, 1H), 7.08-7.16 (m, 2H), 5.44 (d, 1H, J = 12.4 Hz, C*H*$_2$Bt-1), 5.30 (d, 1H, J = 12.4 Hz, C*H*$_2$Bt-1), 3.07 (dd, 1H, J_1 = 3.4 Hz, J_2 = 6.7 Hz), 2.19 (d, 1H, J = 3.2 Hz, *trans*-H to methine), 2.18 (d, 1H, J = 6.6 Hz, *cis*-H to methine); ^{13}C nmr: δ 157.3, 149.8, 149.0, 145.9, 136.4, 127.6, 124.0, 122.2, 120.5, 119.7, 109.9, 69.4, 40.4, 35.3.

Anal. Calcd. for $C_{14}H_{13}N_5$: C, 66.92; H, 5.21; N, 27.87. Found: C, 66.81; H, 5.16; N, 27.78.

1-(Benzotriazol-2-yl)-2-(pyrid-2-yl)ethane (**5a**).

This compound was obtained as a light yellow oil; ^{1}H nmr: δ 8.57 (m, 1H, α-pyridyl), 7.85-7.82 (m, 2H, 4- and 7-H, Bt-2), 7.51-7.45 (dt, 1H, J_1 = 1.8 Hz, J_2 = 7.7 Hz, γ-pyridyl), 7.37-7.31 (m, 2H, 6- and 7-H, Bt-2), 7.09-7.08 (m, 1H, β-pyridyl), 7.03 (d, 1H, J = 7.8 Hz, β'-pyridyl), 5.20 (t, 2H, J = 7.3 Hz), 3.63 (t, 2H, J = 7.3 Hz). ^{13}C nmr: δ 157.0, 149.2, 144.0, 136.2, 125.9, 123.0, 121.6, 117.7, 55.4, 37.7.

Anal. Calcd. for $C_{13}H_{12}N_4$: C, 69.62; H, 5.39; N, 24.98. Found: C, 69.29; H, 5.34; N, 25.32.

1-(5-Phenyl- 1,2,3,4-tetrazol-1-yl)-2-(pyrid-2-yl)aziridine (**4b**).

This compound was obtained as a light yellow oil; ^{1}H nmr: δ 8.52 (d, 1H, J = 4.7 Hz, α-pyridyl), 8.18-8.15 (m, 2H), 7.59 (dt, 1H, J_1 = 1.8 Hz, J_2 = 7.6 Hz, γ-pyridyl), 7.50-7.43 (m, 4H), 7.23 (d, 1H, J = 7.7 Hz, β'-pyridyl), 5.51 (d, 1H, J = 11.9 Hz, C*H*$_2$Bt-1), 5.36 (d, 1H, J = 12.0 Hz, C*H*$_2$Bt-1), 3.08 (dd, 1H, J_1 = 3.5 Hz, J_2 = 6.5 Hz), 2.28 (d, 1H, J = 3.5 Hz, *trans*-H to methine), 2.19 (d, 1H, J = 6.7 Hz, *cis*-H to methine); ^{13}C nmr: δ 149.1, 136.4, 130.3, 128.7, 128.6, 126.8, 122.3, 120.7, 72.4, 39.8, 34.6.

Anal. Calcd. for $C_{15}H_{14}N_6$: C, 64.73; H, 5.07; N, 30.20. Found: C, 65.00; H, 5.13; N, 30.08.

1-(5-Phenyl-1,2,3,4-tetrazol-1-yl)-2-(pyrid-2-yl)ethane (**5b**).

This compound was obtained as a light yellow oil; ^{1}H nmr: δ 8.56 (dd, 1H, J_1 = 0.8 Hz, J_2 = 4.9 Hz, α-pyridyl), 8.14-8.10 (m, 2H), 7.55 (dt, 1H, J_1 = 1.8 Hz, J_2 = 7.6 Hz, γ-pyridyl), 7.49-7.43 (m, 3H), 7.15-7.11 (m, 1H, β-pyridyl), 7.08 (d, 1H, J = 7.7 Hz, β'-pyridyl), 5.10 (t, 2H, J = 7.3 Hz), 3.54 (t, 2H, J = 7.3 Hz); ^{13}C nmr: δ 164.8, 156.4, 149.5, 136.4, 130.1, 128.8, 128.7, 126.6, 123.2, 121.9, 52.1, 37.1.

Anal. Calcd. for $C_{14}H_{13}N_5$: C, 66.92; H, 5.21; N, 27.87. Found: C, 66.69; H,5 .15; N, 27.96.

Reaction of Azides **1a,b** with 1-Vinylpyrrolid-2-one and with 1-Vinylcarbazole.

A mixture of azide **1a** or **1b** (1.5 mmoles) and the appropriate dienophile (2 mmoles) in toluene (50 ml) was refluxed for 24 hours. The solvent was removed *in vacuo* to give crude compounds **6a**, **6b**, and **6c** in 75%, 83% and 80% yields, respectively.

1-(Benzotriazol-1-ylmethyl)-5-(pyrrolid-2-on-1-yl)-Δ^2-1,2,3-triazoline (**6a**).

This compound was obtained as colorless plates (ethyl alcohol), mp 155-156°; ^{1}H nmr: δ 8.04 (d, 1H, J = 8.4 Hz), 7.90 (d, 1H, J = 8.4 Hz), 7.58-7.53 (m, 1H), 7.44-7.38 (m, 1H), 6.53 (s, 2H), 6.06 (dd, 1H, J_1 = 3.3 Hz, J_2 = 9 .9 Hz), 4.25 (dd, 1H, J_1 = 3.3 Hz, J_2 = 17.6 Hz), 4.11 (dd, 1H, J_1 = 9.9 Hz, J_2 = 17.6 Hz), 2.81-2.74 (m, 1H), 2.39-2.18 (m, 2H), 1.80-1.64 (m, 2H), 1.48-1.32 (m, 1H); ^{13}C nmr: δ 175.6, 145.8, 132.5, 128.0, 124.3, 119.6, 110.2, 67.6, 60.7, 57.6, 41.4, 30.1, 16.7.

Anal. Calcd. for $C_{13}H_{15}N_7O$: C, 54.73; H, 5.30; N, 34.37. Found: C, 54.38; H, 5.26; N, 34.64.

1-(Benzotriazol-1-ylmethyl)-5-(carbazol-9-yl)-Δ^2-1,2,3-triazoline (**6b**).

This compound was obtained as light yellow needles (benzene-hexane, 1:1), mp 156-158° (benzene-hexane, 1:1); ^{1}H nmr: δ 8.07-8.04 (m, 2H), 8.00-7.96 (m, 1H), 7.63-7.60 (m, 1H), 7.49-7.24 (m, 8H), 6.45 (d, 1H, J = 15.2 Hz, C*H*$_2$Bt), 6.40 (dd, 1H, J_1 = 5.6 Hz, J_2 = 12.0 Hz), 5.85 (d, 1H, J = 15.2 Hz, C*H*$_2$Bt), 4.67 (dd, 1H, J_1 = 5.6 Hz, J_2 = 18.5 Hz), 4.45 (dd, 1H, J_1 = 12.0 Hz, J_2 = 18.5 Hz); ^{13}C nmr: δ 146.1, 132.3, 128.1, 126.4, 124.4, 120.7, 120.6, 119.9, 109.7, 69.0, 62.4, 56.9.

Anal. Calcd. for $C_{21}H_{17}N_7$: C, 68.65; H, 4.66; N, 26.69. Found: C, 68.96; H, 4.74; N, 26.58.

1-(5-Phenyl-1,2,3,4-tetrazol-1-ylmethyl)-5-(pyrrolid-2-on-1-yl) -Δ^2-1,2,3triazoline (**6c**).

This compound was obtained as light yellow prisms (benzene-hexane, 1:1), mp 98-101°; ^{1}H nmr: δ 8.18-8.15 (m, 2H), 7.51-7.48 (m, 3H), 6.53 (d, 1H, J = 14.6 Hz, C*H*$_2$Bt), 6.46 (d, 1H, J = 14.6 Hz C*H*$_2$Bt), 6.11 (dd, 1H, J_1 = 3.3 Hz, J_2 = 9.9 Hz), 4.32 (dd, 1H, J_1 = 3.5 Hz, J_2 = 17.8 Hz), 4.20 (dd, 1H, J_1 = 9.9 Hz, J_2 = 17.8 Hz), 3.00-2.92 (m, 1H), 2.78-2.23 (m, 3H), 1.90-1.75 (m, 1H), 1.73-1.55 (m, 1H); ^{13}C nmr: δ 175.6, 165.4, 130.5, 128.8, 126.7, 126.6, 67.9, 62.1, 60.5, 41.5, 30.2, 16.9.

Anal. Calcd. for $C_{14}H_{16}N_8O$: C, 53.84; H, 5.16; N, 35.88. Found: C, 54.17; H, 5.17; N, 35.76.

Synthesis of Adducts **7, 8, 9, 10** and **11**.

A mixture of azide **1a** or **1b** (5.7 mmoles) and the appropriate dienophile (7.5 mmoles) in toluene (30 ml) was refluxed for 24 hours for adducts **7, 8,** and **10** and **11**, and 3 hours for adduct **9**. The solvent was removed in *vacuo* to give a residue which crystallized on addition of a few drops of diethyl ether, and then was recrystallized from ethyl alcohol to give **7** (85% yield), **8** (65% yield), **9** (80% yield), and a mixture of **10** and **11** (4:1) (80% yield).

1-(Benzotriazol-1-ylmethyl)-4,7-methano-3a,4,5,6,7,7a-hexahydro-1*H*-benzotriazole (**7**).

This compound was obtained as colorless plates, mp 128-130°; ^{1}H nmr: δ 8.05 (d, 1H, J = 8.5 Hz), 7.75 (d, 1H, J = 8.2 Hz), 7.51 (dd, 1H, J_1 = 7.4 Hz, J_2 = 7.8 Hz), 7.40 (dd, 1H, J_1 = 7.4 Hz, J_2 = 7.9 Hz), 6.53 (d, 1H, J = 14.8 Hz, C*H*$_2$Bt), 6.35 (d, 1H, J = 14.8 Hz, C*H*$_2$Bt), 4.31 (d, 1H, J = 9.3 Hz, 4-H), 3.23 (d, 1H, J = 9.3 Hz, 5-H), 2.65-2.62 (m, 1H), 2.23-2.20 (m, 1H), 1.50-1.44 (m, 2H), 1.23-1.13 (m, 2H), 1.04 (dd, 1H, J_1 = 1.3 Hz, J_2 = 10.5 Hz, *anti* of bridge), 0.91 (dd, 1H, J_1 = 1.5 Hz, J_2 = 10.7 Hz, *syn* of bridge); ^{13}C nmr: δ 146.3, 132.3, 128.0, 124.4, 119.8, 110.3, 88.2, 59.83, 59.78, 41.1, 40.5, 32.2, 25.6, 24.4.

Anal. Calcd. for $C_{14}H_{16}N_6$: C, 62.69; H, 5.97; N, 31.34. Found: C, 62.90; H, 6.03; N, 31.26.

Inseparable Mixture of *exo* and *endo* Isomers (2.5:1) of Adduct **8**.

This mixture was obtained as colorless plates, mp 133-135°; ^{1}H nmr (the signals of the minor isomer are in square brackets): δ 8.06 (d, 1H, J = 8.3 Hz) [8.06 (d, 1H, J = 8.3 Hz)], 7.77-7.74 (m, 1H) [7.77-7.74 (m, 1H)], 7.53-7.50 (m, 1H) [7.53-7.50 (m, 1H)], 7.48-7.37 (m, 1H), [7.48-7.37 (m, 1*H*)], 6.48 (d, 1H, J = 14.8 Hz, C*H*$_2$Bt) [6.50 (d, 1H, J = 14.9 Hz, C*H*$_2$Bt)], 6.37 (d, 1H, J = 14.9 Hz, C*H*$_2$Bt) [6.35 (d, 1H, J = 14.9 Hz, C*H*$_2$Bt)], 5.60-5.50 (m, 2H) [5.60-5.50 (m, 2H)], 4.32 (d, 1H, J = 9.6 Hz) [4.28 (d, 1H, J = 9.6 Hz)], 3.18 (d, 1H, J = 9.6 Hz) [3.25 (d, 1H, J = 9.6 Hz)], 3.13-3.08 (m, 1H) [3.13-3.08 (m, 1H)], [2.76 (d, 1H, J = 5.3 Hz)], 2.60-2.50 (m, 1H) [2.60-2.50 (m, 1H)], 2.34 (d, 1H, J = 4.7 Hz), 2.30-2.20 (m, 3H) [2.30-2.20 (m, 2H)], [2.11 (d, 1H, J = 4.4 Hz)], 1.26-1.18 (m, 1H) [1.26-1.18 (m, 1H)], 1.00-0.94 (m, 1H) [1.00-0.94 (m, 1H)]; ^{13}C nmr (some signals are coalesced): δ 146.2, 132.3, 131.6, 131.2, 130.82, 130.78, 127.9, 124.3, 119.7, 110.23, 110.21, 85.4, 82.2, 59.8, 59.7, 57.2, 54.5, 51.4, 51.1, 46.0, 45.2, 44.2, 43.5, 40.7, 40.3, 34.9, 34.7, 32.0, 31.7, 30.8.

Anal. Calcd. for $C_{17}H_{18}N_6$: C, 66.65; H, 5.92; N, 27.43. Found: C, 66.52; H, 5.96; N, 27.07.

1-(Benzotriazol-1-ylmethyl)-5-methyl-1,3a,4,5,6,6a-hexahydro-3a,6a-*cis*-pyrrolo[3,4-*d*]-1,2,3-triazole-4,6-dione (**9**).

This compound was obtained as light yellow prisms, mp 133-135°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 8.11 (d, 1H, J = 8.4 Hz), 7.92 (d, 1H, J = 8.4 Hz), 7.64-7.61 (m, 1H), 7.49-7.46 (m, 1H), 7.00 (d, 1H, J = 15.4 Hz, C*H*$_2$Bt), 6.53 (d, 1H, J = 15.4 Hz, C*H*$_2$Bt), 5.70 (d, 1H, J = 10.5 Hz), 4.40 (d, 1H, J = 10.5 Hz), 2.80 (s, 3H); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 172.4, 170.5, 145.3, 132.5, 127.9, 124.4, 119.3, 110.5, 84.2, 59.2, 56.7, 24.7.

Anal. Calcd-for $C_{12}H_{11}N_7O_2$: C, 50.53; H, 3.89; N, 34.37. Found C, 50.52; H, 3.89; N, 34.66.

6-(Benzotriazol-1-ylmethyl)-3-methyl-3,6-azabicyclo[3.1.0]-hexane-2,4-dione (**10**) and 3-(Benzotriazol-1-ylmethylamino)-1-methyl-3-pyrroline-2,5-dione (**11**).

This mixture was obtained as colorless plates, mp 168-170°; ^{1}H nmr (dimethyl sulfoxide-d_6) (the signals of **11** are in square brackets): δ [8.98-8.90 (broad m, 1H, NH)], 8.15-8.11 (m, 1H), [8.15-8.11 (m, 1H)], 8.07-8.04 (m, 1H), [8.07-8.04 (m, 1H)], 7.86-7.62 (m, 1H), [7.86-7.62 (m, 1H)], 7.52-7.44 (m, 1H), [7.52-7.44 (m, 1H)], [6.14 (d, 2H, J = 5.8 Hz, CH_2Bt)], 5.50 (s, 2H, CH_2Bt), [5.31 (s, 1H)], 3.88 (s, 2H), [2.79 (s, 3H)], 2.68 (s, 3H); ^{13}C nmr (dimethyl sulfoxide-d_6) (the signals of **11** are in parentheses): δ 171.6, (166.8, 148.5), 145.4, (145.4), 132.5, (131.6), 128.1, (127.9), 124.4, (124.4), 119.3, (119.3, 110.8), 110.7, (88.0), 65.8, (65.8, 55.6), 23.9, (23.6).

Anal. Calcd. for $C_{12}H_{11}N_5O_2$: C, 56.03; H, 4.31; N, 27.22. Found: C, 56.14; H, 4.31; N, 27.52.

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