

Pyridazines. LXX. Reactions of Azidoazolopyridazines  
with Unsaturated Compounds

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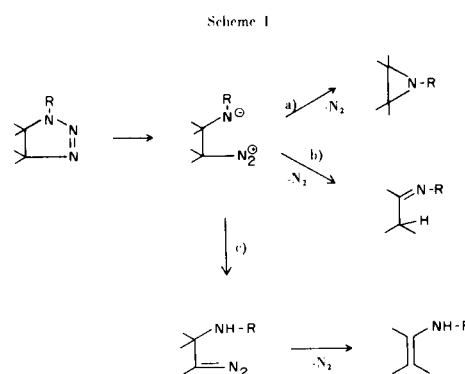
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Cycloaddition reactions of azidoazolopyridazines with unsaturated esters, cyclic enol ethers, styrene, 2-vinyl-pyridine, bicyclo[2.2.1]heptene, dicyclopentadiene and dehydrobenzene were investigated. The reaction proceeded *via* the intermediate  $\Delta^2$ -1,2,3-triazolines which were in most cases thermolabile and decomposed further to give the final products which were enamines, imines of fused aziridines.

Although 1,3-dipolar cycloadditions have been known for some time (1), the concept and the generality of the reaction were fully presented by Huisgen and his school (2). Azides represent a class of reactive 1,3-dipoles and their addition to polarophiles has been reviewed (2-4). However, these investigations were limited almost exclusively to aryl and sulphonyl azides. Later, orbital symmetry considerations were found to be of great value for concerted cycloadditions (5-7). The observed supra-suprafacial additions, almost no solvent dependence of the reaction rates and dependence on steric effects are in favour for the generally accepted interpretation of a concerted process of 1,3-dipolar cycloadditions (8).

The cycloaddition products of azides to olefins are of variable thermal lability. The decomposition products of these  $\Delta^2$ -1,2,3-triazolines are dealt with in detail in a review (9). The resulting products are aziridines, imines, diazoalkanes or products which are formed from these compounds by subsequent processes (Scheme 1). Our interest in azidoazolopyridazines, in particular in azido-tetrazolo isomerizations (10), prompted us to investigate their addition to unsaturated systems and to compare their behaviour with that of arylazides and some azidoazines (11).

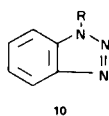
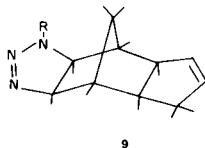
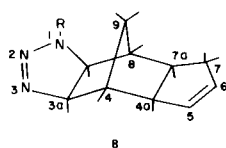
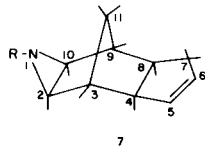
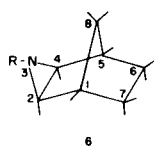
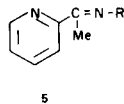
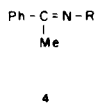
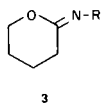
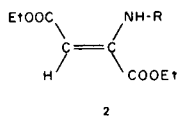
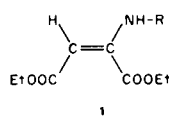
Since conjugation of a double bond with carbalkoxy or phenyl groups is expected to enhance its reactivity towards an azide, we have employed several activated unsaturated systems. When diethyl maleate or fumarate were treated with azidoazolopyridazines the corresponding aminomaleate (1) or aminofumarate (2) were obtained. It is noteworthy that the reaction took place with retention of the configuration. This is understandable, since the reaction can be interpreted as cycloaddition with subsequent decomposition of the triazoline into an



unstable diazoester. This, after elimination of nitrogen, is transformed into the corresponding enamino compound (Scheme 1, path c). Similar transformations of azides in the presence of unsaturated esters have been observed before (11, 12, 13).

In a similar manner occurred the reaction with a cyclic enol ether (Scheme 1, path b). The initially formed triazolines decomposed at 90-95° into an imine and nitrogen. Thus, in all cases when 3,4-dihydro-2H-pyran was treated with the corresponding heterocyclic azide the imino compounds (3) were isolated. With complex azides, where azido-tetrazolo equilibration takes place in solution (14), a mixture of the possible isomers was obtained. In this manner, 6-azidopyrido[4,3-d]tetrazolo[1,5-b]pyridazine afforded after 1 hour at 90° a mixture of 3g and 3h in the ratio of 3:1, whereas 6-azidopyrido[2,3-d]tetrazolo[1,5-b]pyridazine was transformed after 3 hours at 90° into a mixture of 3e and 3f in the ratio of 1:1.

When the reaction was performed with styrene and 2-vinylpyridine, it proceeded in the anticipated manner. The intermediate triazolines again could not be isolated



and their decomposition products, the Schiff bases (4,5) were obtained in moderate yield.

Since it is known that strained unsaturated systems undergo cycloaddition reactions with greater ease, bicyclo[2.2.1]heptene and dicyclopentadiene were reacted with azidoazolopyridazines. Cycloadditions of azides to such systems involve a relatively low enthalpy of activation. The products, which we have isolated were fused aziridines (6,7) indicating thermal lability of the intermediate triazolines. The failure to obtain these  $\Delta^2$ -1,2,3-triazolines as cycloadducts is in accord with the observation that electronwithdrawing substituents at N<sub>1</sub> of the triazoline ring enhance thermal instability (9). However, in the case of 6-azidoimidazo[1,2-*b*]pyridazine and dicyclopentadiene it was possible to obtain the corresponding fused triazoline (8a). It is thermally quite stable, but upon irradiation it was transformed into the corresponding aziridine (7a).

The structure of these triazoline and aziridine derivatives are supported by nmr spectra. It is known that only exo protons of the bicycloheptane ring are coupled with the bridgehead protons at C<sub>4</sub> and C<sub>7</sub> (15,16). The protons of the aziridine ring, H<sub>2</sub> and H<sub>4</sub>, of 6 appear in

nmr spectrum as sharp singlet in the range 6.92-7.79  $\tau$ . No further splitting is observed and this is in agreement with the endo-position of these two protons. As a consequence of shielding by the aziridine ring  $\tau$ -values for these two protons are expected to be greater than those for H<sub>1</sub> and H<sub>5</sub>. In fact, this is observed with phenyl substituent, but the heteroaromatic substituents decrease the electron density of the aziridine nitrogen inasmuch that an opposite situation is observed, i.e.  $\tau$  H<sub>1</sub>H<sub>5</sub> >  $\tau$  H<sub>2</sub>H<sub>4</sub>.

The protons of the triazoline ring in the cycloadduct with dicyclopentadiene (8a) are symmetrical doublets centered at 5.40 and 6.09  $\tau$ , corresponding to H<sub>3a</sub> and H<sub>8a</sub>, and are coupled with  $J = 8.8$  Hz. For correlation purposes, the adduct with phenyl azide (8i) was prepared (17) and its nmr spectrum shows similar pattern as above. Moreover, the signal for H<sub>3a</sub> in 8i is quartet with  $J_{3a,8a}$

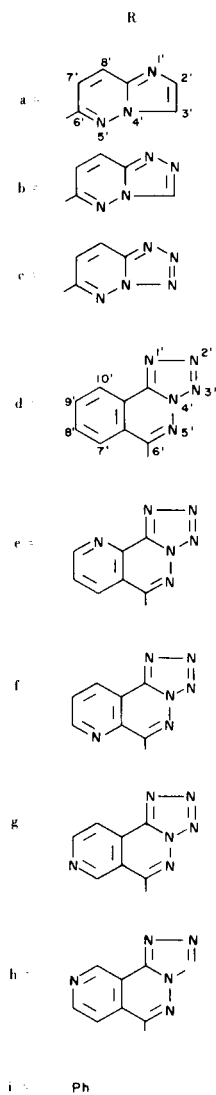


Table I

Compound No.	Yield %	M.p. °C	Crystallized from	Formula	Analytical data		Nmr data
					Calculated	Found	
<b>1c</b>	16	145-147	ethanol	$C_{12}H_{14}N_6O_4$	N 27.44	N 27.44	DMSO-d <sub>6</sub> : 2.22 (d, H <sub>7</sub> '), 1.42 (d, H <sub>8</sub> '), 4.10 (s, =CH), 5.80 and 5.82 (q, CH <sub>2</sub> CH <sub>3</sub> ), 8.75 and 8.88 (t, CH <sub>2</sub> CH <sub>3</sub> ), 0.30 (broad, NH); J <sub>7,8</sub> ' = 9.5, J <sub>Et</sub> = 6.8 Hz.
<b>2c</b>	42	183	ethanol	$C_{12}H_{14}N_6O_4$	C 47.05 H 4.60 N 27.44	C 47.21 H 4.77 N 27.70	DMSO-d <sub>6</sub> : 2.65 (d, H <sub>7</sub> '), 1.60 (d, H <sub>8</sub> '), 4.05 (s, =CH), 5.58 and 5.72 (q, CH <sub>2</sub> CH <sub>3</sub> ), 8.62 (t, CH <sub>2</sub> CH <sub>3</sub> ), 0.0 (broad, NH); J <sub>7,8</sub> ' = 9.5, J <sub>Et</sub> = 6.8 Hz.
<b>3d</b>	78	194	ethanol and DMF	$C_{13}H_{12}N_6O$ (a)	N 31.31	N 31.59	DMSO-d <sub>6</sub> : 1.50 and 2.10 (m, H <sub>7</sub> 'H <sub>8</sub> 'H <sub>9</sub> 'H <sub>10</sub> '), 7.10 (m, 3-CH <sub>2</sub> ), 5.83 (m, 6-CH <sub>2</sub> ), 8.20 (m, 4- and 5-CH <sub>2</sub> )
<b>4c</b>	24	136-138	CHCl <sub>3</sub> and petrolether	$C_{12}H_{10}N_6$ (b)	N 35.28	N 35.46	Deuteriochloroform: 2.6 (d, H <sub>7</sub> '), 1.5 (d, H <sub>8</sub> '), 7.5 (s, Me), 1.80 and 2.35 (m, C <sub>6</sub> H <sub>5</sub> ); J <sub>7,8</sub> ' = 9.7 Hz.
<b>4g</b>	39	162	ethanol	$C_{15}H_{11}N_7$ (c)	N 33.89	N 33.67	DMSO-d <sub>6</sub> : 0.15 (d, H <sub>7</sub> '), 0.55 (dd, H <sub>9</sub> '), 1.52 (dd, H <sub>10</sub> '), 7.40 (s, Me), 1.90 and 2.50 (m, C <sub>6</sub> H <sub>5</sub> ); J <sub>9,10</sub> ' = 5.7, J <sub>7,10</sub> ' = 0.8 Hz.
<b>6b</b>	50	175-178	ethanol	$C_{12}H_{13}N_5$ (d)	C 63.42 H 5.77 N 30.82	C 63.44 H 5.73 N 30.96	Deuteriochloroform: 7.25 (s, H <sub>2,4</sub> ), 7.38 (s, H <sub>1,5</sub> ), 8.45 (d, H <sub>8</sub> syn), 9.10 (d, H <sub>8</sub> anti), 1.21 (s, H <sub>3</sub> '), 3.15 (d, H <sub>7</sub> '), 2.17 (d, H <sub>8</sub> '); J <sub>8,9</sub> = 9.9, J <sub>7,8</sub> ' = 9.8 Hz.
<b>6d</b>	40	228-230	ethanol	$C_{15}H_{14}N_6$ (e)	C 64.73 H 5.07 N 30.20	C 64.96 H 5.33 N 30.14	Deuteriochloroform: 6.92 (s, H <sub>2,4</sub> ), 7.23 (s, H <sub>1,5</sub> ), 8.18 (d, H <sub>8</sub> syn), 8.93 (d, H <sub>8</sub> anti), 1.75 (m, H <sub>7</sub> '), 2.02 (m, H <sub>8</sub> ' and H <sub>9</sub> '), 1.36 (m, H <sub>10</sub> '); J <sub>8,9</sub> = 10.6 Hz.
<b>6a</b>	14	72-72	(f)	$C_{13}H_{14}N_4$	C 69.00 H 6.24 N 24.76	C 69.08 H 6.34 N 24.52	Deuteriochloroform: 7.19 (s, H <sub>2,4</sub> ), 7.28 (s, H <sub>1,5</sub> ), 8.4 (d, H <sub>8</sub> syn), 9.11 (d, H <sub>8</sub> anti), 2.28 (m, H <sub>2,3</sub> 's'), 3.15 (d, H <sub>7</sub> '); J <sub>8,9</sub> = 10.1, J <sub>7,8</sub> ' = 9.3 Hz.
<b>7c</b>	39	195-197	ethanol	$C_{14}H_{14}N_6$ (g)	C 63.14 H 5.30 N 31.56	C 63.40 H 5.31 N 31.33	Deuteriochloroform: 4.37 (s, H <sub>5,6</sub> ), 6.8 (s, H <sub>8</sub> ), 8.31 (d, H <sub>11</sub> syn), 8.85 (d, H <sub>11</sub> anti), 2.77 (d, H <sub>7</sub> '), 1.92 (d, H <sub>8</sub> '); J <sub>11,11</sub> = 11.3, J <sub>7,8</sub> ' = 9.4 Hz.
<b>7b</b>	40	207-209	ethanol	$C_{15}H_{15}N_5$ (h)	C 67.90 H 5.70 N 26.40	C 67.55 H 5.39 N 26.37	Deuteriochloroform: 4.34 (s, H <sub>5,6</sub> ), 6.8 (s, H <sub>8</sub> ), 8.30 (d, H <sub>11</sub> syn), 8.86 (d, H <sub>11</sub> anti), 1.13 (s, H <sub>3</sub> '), 2.11 (d, H <sub>8</sub> '), 3.12 (d, H <sub>7</sub> '); J <sub>11,11</sub> = 10.4, J <sub>7,8</sub> ' = 10.1 Hz.
<b>7d</b>	27	210-213	ethanol	$C_{18}H_{16}N_6$ (i)	C 68.33 H 5.10 N 26.57	C 68.27 H 5.36 N 26.35	Deuteriochloroform: 4.38 (s, H <sub>5,6</sub> ), 6.7 (s, H <sub>8</sub> ), 8.09 (d, H <sub>11</sub> syn), 8.74 (d, H <sub>11</sub> anti), 1.40 (m, H <sub>10</sub> '), 1.75 (m, H <sub>7</sub> '), 2.0 (m, H <sub>8</sub> 's'); J <sub>11,11</sub> = 10.0 Hz.

(a) Mass spectrum: M<sup>+</sup> = 268. (b) Mass spectrum: M<sup>+</sup> = 238. (c) Mass spectrum: M<sup>+</sup> = 289. (d) Mass spectrum: M<sup>+</sup> = 278. (e) The compound was purified by tlc on silica, using solvent mixture of chloroform, ethanol and petrolether, 80:50:14, and eluted with chloroform. The product was dissolved in a minimum amount of chloroform and the solution poured into petrolether; mass spectrum: M<sup>+</sup> = 226. (f) Mass spectrum: M<sup>+</sup> = 226. (g) Mass spectrum: M<sup>+</sup> = 226. (h) Reaction time 6 hours; mass spectrum: M<sup>+</sup> = 265. (i) Mass spectrum: M<sup>+</sup> = 316.

= 9.6 and another  $J = 3.4$  Hz. This is ascribed to a long range coupling with  $H_{4a}$ . Since such coupling is not observed in the addition product of phenyl azide with bicyclo[2.2.1]heptene (18),  $H_{3a}$  and  $H_{4a}$  have to be similarly oriented in relation to the central bridge  $C_4-C_8$ . This suggests that the  $N = N$  and  $C = C$  bonds should be oriented as in **8** and not as in **9**.

Finally, it could be demonstrated that 6-azidotetrazolo[1,5-*b*]-pyridazine reacted readily with the highly reactive dehydrobenzene to give the benzotriazole derivative (**10c**). This parallels the reactivity of aromatic azides (19) and contrasts the failure of cycloaddition of some heterocyclic azides (20).

On the basis of the above observations, it can be concluded that reactions of azidoazolopyridazines follow, in general, the common pattern of reactivity of aromatic azides. There are, however, different decomposition paths of the intermediate triazolines as concluded from the structures of the obtained products.

#### EXPERIMENTAL

All nmr spectra were obtained on a Jeol JNM C60-HL spectrometer and mass spectra were recorded on a Hitachi-Perkin-Elmer RMU-6L instrument. A Rayonet photochemical reactor was used for irradiations. Thin layer chromatography (tlc) was carried out on Kieselgel F-254 plates purchased from Merck.

Starting materials.

The preparation of azidoazolopyridazines was reported previously: 6-azidoimidazo[1,2-*b*]pyridazine (21), 6-azido-*s*-triazolo[4,3-*b*]- and 6-azidotetrazolo[1,5-*b*]pyridazine (22), 6-azidopyrido[4,3-*d*]tetrazolo[1,5-*b*]pyridazine (23) and 6-azidopyrido[2,3-*d*]tetrazolo[1,5-*b*]pyridazine (14). The adduct of phenyl azide with dicyclopentadiene (**8**) was prepared according to Alder and Stein (17), m.p. 130°; nmr (deuteriochloroform):  $\tau = 5.65$  (q,  $H_{3a}$ ), 6.35 (d,  $H_{8a}$ ), 4.41 (s,  $H_5H_6$ ), 2.89 (m,  $C_6H_5$ ), 8.70 (d,  $H_9$  *syn*), 8.83 (d,  $H_9$  *anti*);  $J_{3a8a} = 9.6$ ,  $J_{3a4a} = 3.2$ ,  $J_{9,9} = 10.8$  Hz.

Diethyl(*s*-Triazolo[4,3-*b*]pyridazinyl-6')-aminomaleate (**1b**).

A mixture of 6-azido-*s*-triazolo[4,3-*b*]pyridazine (1.6 g.) and diethyl maleate (4 ml.) was heated at 140° for 3 hours. Upon cooling, some ethyl acetate was added, the reaction mixture was filtered and upon evaporation *in vacuo* the product obtained was crystallized from water, m.p. 125-127° (yield 0.97 g., 32%); nmr (deuteriochloroform):  $\tau = 1.28$  (s,  $H_3'$ ), 3.08 (d,  $H_7'$ ), 2.02 (d,  $H_8'$ ), 4.30 (s, =CH), 5.70 and 5.82 (q,  $CH_2CH_3$ ), 8.68 and 8.72 (t,  $CH_2CH_3$ ), 0.0 (broad, NH);  $J_{7'8'} = 9.5$ ,  $J_{El} = 6.8$  Hz.

Anal. Calcd. for  $C_{13}H_{15}N_5O_4$ : C, 51.14; H, 4.95; N, 22.94. Found: C, 51.26; H, 5.09; N, 23.10.

In a similar manner were prepared compound **1c** and **2c** (Table 1).

6-(Tetrahydropyrimino-2')tetrazolo[1,5-*b*]pyridazine (**3c**).

A mixture of 6-azidotetrazolo[1,5-*b*]pyridazine (0.81 g.) and 3,4-dihydro-2*H*-pyran (10 ml.) was heated at 90° for 2 hours. Upon cooling, the separated product was filtered off and dried. On attempted crystallization the product hydrolyzed, m.p. 126°

(yield 0.925 g., 85%); mass spectrum:  $M^+$  218; nmr (DMSO- $d_6$ ):  $\tau = 1.40$  (d,  $H_8'$ ), 2.50 (d,  $H_7'$ ), 6.60 (m, 3'- $CH_2$ ), 5.70 (m, 6'- $CH_2$ ), 8.25 (m, 4'- and 5'- $CH_2$ ).

Anal. Calcd. for  $C_9H_{10}N_6O$ : N, 38.52. Found: N, 38.40.

In a similar manner, compound **3d** was obtained after 5 hours (Table 1).

If the reaction was performed with 6-azidopyrido[4,3-*d*]tetrazolo[1,5-*b*]pyridazine (1 hour reaction time) and 6-azidopyrido[2,3-*d*]tetrazolo[1,5-*b*]pyridazine (3 hours reaction time), in both cases azido-tetrazolo isomerization took place (14) and the reaction mixture consisted on the basis of nmr examination of compounds **3g** and **3h** (3:1 ratio) or **3e** and **3f** (1:1 ratio), respectively; nmr: compound **3g** (DMSO- $d_6$ ):  $\tau = 0.17$  (s,  $H_7'$ ), 0.65 (d,  $H_9'$ ), 1.45 (d,  $H_{10}'$ );  $J_{9,10} = 5.7$  Hz. Compound **3h** (DMSO- $d_6$ ):  $\tau = 0.72$  (d,  $H_7'$ ), 1.60 (d,  $H_8'$ ), 0.0 (s,  $H_{10}'$ ),  $J_{7'8'} = 6.0$  Hz. Compound **3f** (DMSO- $d_6$ ):  $\tau = 0.80$  (dd,  $H_8'$ ), 1.85 (dd,  $H_9'$ ), 1.05 (dd,  $H_{10}'$ );  $J_{8'9'} = 5.5$ ,  $J_{9'10'} = 8.0$ ,  $J_{8'10'} = 1.8$  Hz. Compound **3e** (DMSO- $d_6$ ):  $\tau = 1.37$  (dd,  $H_7'$ ), 2.05 (dd,  $H_8'$ ), 0.75 (dd,  $H_9'$ ),  $J_{7'8'} = 8.0$ ,  $J_{8'9'} = 5.5$ ,  $J_{7'9'} = 1.8$  Hz. In all compounds signals of the pyran ring appear at 5.5 (m, 3- $CH_2$ ), 8.35 (m, 4- and 5- $CH_2$ ), 5.80 (m, 6- $CH_2$ ).

6-(1'-Methylbenzylideneamino)-*s*-triazolo[4,3-*b*]pyridazine (**4b**).

A mixture of 6-azido-*s*-triazolo[4,3-*b*]pyridazine (0.805 g.), styrene (1 g.) and toluene (10 ml.) was heated at 125-130° for 25 hours. The reaction mixture was cooled and filtered and the filtrate was evaporated *in vacuo*. The tarry residue was dissolved in chloroform and the solution slowly poured into cold petrol ether. The separated product was filtered off (0.1 g.), m.p. 141-143°; mass spectrum:  $M^+$  237; nmr (deuteriochloroform):  $\tau = 0.7$  (s,  $H_3'$ ), 3.0 (d,  $H_7'$ ), 1.8 (d,  $H_8'$ ), 7.5 (s, Me), 1.80 and 2.35 (m,  $C_6H_5$ );  $J_{7'8'} = 9.5$  Hz.

Anal. Calcd. for  $C_{13}H_{11}N_5$ : N, 29.52. Found: N, 29.70.

Compounds **4c** and **4g** were prepared similarly (Table 1).

Reaction of 6-Azidotetrazolo[5,1-*a*]phthalazine and 2-vinylpyridine.

The azido compound (1.06 g.), 2-vinylpyridine (1.0 g.) and toluene (10 ml.) were heated at 125-130° for 105 hours. Upon cooling and filtration, the filtrate was evaporated to dryness and the residue was dissolved in *N,N*-dimethylformamide and purified by tlc on silica, methanol as solvent. The product (**5d**) was finally crystallized from ethanol and *N,N*-dimethylformamide, 2:1, m.p. 205-207° (yield 45 mg., 3%); mass spectrum:  $M^+$  289; nmr (DMSO- $d_6$ ):  $\tau = 1.0-2.5$  (m, pyridyl and phenyl protons), 7.5 (s, Me).

Anal. Calcd. for  $C_{15}H_{11}N_7$ : N, 33.89. Found: 34.09.

3-(Tetrazolo[1,5-*b*]pyridazinyl-6')-3'-azatricyclo[3,2,1.0<sup>2,4</sup>-*exo*]octane (**6c**).

A mixture of 6-azidotetrazolo[1,5-*b*]pyridazine (0.9 g.), bicyclo[2.2.1]heptene (norbornene) (0.45 g.) and ethanol (15 ml.) was heated under reflux for 4 hours. The solvent was evaporated and the residue was crystallized from ethanol, m.p. 157-159° (0.5 g., 39% yield); mass spectrum:  $M^+$  228; nmr (deuteriochloroform):  $\tau = 7.08$  (s,  $H_2H_4$ ), 7.34 (s,  $H_1H_5$ ), 8.21 (d,  $H_8$  *syn*), 9.03 (d,  $H_8$  *anti*), 2.79 (d,  $H_7'$ ), 1.96 (d,  $H_8'$ );  $J_{8,8} = 8.2$ ,  $J_{7'8'} = 10.0$  Hz.

Anal. Calcd. for  $C_{11}H_{12}N_6$ : C, 57.88; H, 5.30; N, 36.82. Found: C, 58.03; H, 5.35; N, 36.72.

In a similar manner compounds **6a**, **6b**, **6d**, **7b**, **7c** and **7d** (Table 1) were prepared.

Preparation of Compound **7i**.

The adduct of phenyl azide to dicyclopentadiene (**17**) (**8i**) (0.4 g.) was dissolved in ethanol (15 ml.) and the solution was irradiated ( $\lambda = 300$  nm) in a photochemical reactor for 4 hours. The solvent was then evaporated and the residue crystallized from ethanol, m.p.  $60^\circ$  (yield 0.2 g., 56%); mass spectrum:  $M^+$  223; nmr (deuteriochloroform):  $\tau = 2.8-3.4$  (m,  $C_6H_5$ ), 4.51 (s,  $H_5H_6$ ), 6.9 (s,  $H_8$ ), 8.30 (d,  $H_{11}$  *syn*), 9.00 (d,  $H_{11}$  *anti*);  $J_{11,11} = 10.0$  Hz.

*Anal.* Calcd. for  $C_{16}H_{17}N$ : C, 86.05; H, 7.67; N, 6.27. Found: C, 86.05; H, 7.41; N, 6.40.

Preparation of the Cycloadduct **8a** from 6-Azidoimidazo[1,2-*b*]pyridazine and Dicyclopentadiene.

A mixture of the azide (1.0 g.), dicyclopentadiene (1 ml.) and ethanol (25 ml.) was heated under reflux for 8 hours. The solvent was evaporated and the residue crystallized from ethanol, m.p.  $160^\circ$  dec., (yield 0.5 g., 27%); mass spectrum:  $M^+$  264; nmr (deuteriochloroform):  $\tau = 4.28$  (s,  $H_5H_6$ ), 5.40 (d,  $H_{3a}$ ), 6.09 (d,  $H_{8a}$ ), 8.64 (d,  $H_9$  *syn*), 8.88 (d,  $H_9$  *anti*), 2.1-2.6 (m,  $H_2'H_3'H_8'H_7'$ );  $J_{3a8a} = 8.8$ ,  $J_{9'9} = 11.0$  Hz.

*Anal.* Calcd. for  $C_{16}H_{16}N_6$ : C, 65.73; H, 5.52; N, 28.75. Found: C, 65.77; H, 5.72; N, 28.94.

The triazoline **8a** (150 mg.) when dissolved in ethanol (15 ml.) and irradiated ( $\lambda = 300$  nm) for 2 hours afforded upon evaporation of the solvent an oily residue which crystallized after few days on standing on ice, m.p.  $98-100^\circ$ ; yield of the aziridine **7a**, 0.1 g. (74%); mass spectrum:  $M^+$  264; nmr (deuteriochloroform):  $\tau = 4.51$  (s,  $H_5H_6$ ), 6.9 (s,  $H_8$ ), 8.32 (d,  $H_{11}$  *syn*), 8.97 (d,  $H_{11}$  *anti*), 2.2-2.6 (m,  $H_2'H_3'H_8'H_7'$ ), 3.31 (d,  $H_7'$ );  $J_{11,11} = 10.0$ ,  $J_{7',8'} = 9.4$  Hz.

*Anal.* Calcd. for  $C_{16}H_{16}N_4$ : C, 72.70; H, 6.10; N, 21.10. Found: C, 72.56; H, 5.97; N, 21.19.

6-(Benzotriazolyl-1')tetrazolo[1,5-*b*]pyridazine (**10c**).

A mixture of anthranilic acid (0.15 g.) and acetone (2 ml.) was heated to boil and a mixture of 6-azidotetrazolo[1,5-*b*]pyridazine (0.162 g.) and *n*-amylnitrite (0.117 g.) in dichloromethane (5 ml.) was added dropwise. The product which separated upon cooling (7 mg., 3%) was found to be identical in all respects with the product, prepared by the action of nitrous acid upon 6-(2'-aminoanilino)tetrazolo[1,5-*b*]pyridazine; m.p.  $247-249^\circ$ , mass spectrum:  $M^+$  238; nmr (DMSO- $d_6$ ):  $\tau = 1.20$  (d,  $H_7$ ), 0.90 (d,  $H_8$ ), 1.20-2.40 (m,  $H_4'H_5'H_6'H_7'$ );  $J_{7,8} = 9.2$  Hz.

*Anal.* Calcd. for  $C_{10}H_6N_8$ : C, 50.42; H, 2.52; N, 47.04. Found: C, 50.60; H, 2.74; N, 47.40.

Alternatively, compound **10c** was prepared as follows. A mixture of 6-chlorotetrazolo[1,5-*b*]pyridazine (1.55 g.) and *o*-

phenylenediamine (2.16 g.) was heated at  $120^\circ$  for 45 minutes. The reaction product was treated with ethanol (40 ml.) and heated to boil. Upon filtration and evaporation of the solvent to half of its original volume the product which separated was filtered off and crystallized from ethanol, m.p.  $192-193^\circ$  (yield 1.25 g., 58%); mass spectrum:  $M^+$  227. The compound is 6-(*o*-aminoanilino)-tetrazolo[1,5-*b*]pyridazine.

*Anal.* Calcd. for  $C_{10}H_9N_7$ : C, 52.85; H, 3.99; N, 43.15. Found: C, 52.89; H, 4.25; N, 43.00.

The above compound, when treated with a solution of sodium nitrite and hydrochloric acid is transformed into compound **10c** in 60% yield.

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