Expected Selectivity and Unexpected Isomerization in the Inverse Diels–Alder Reaction of Azolyl Dienes

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Received March 7, 1995[⊗]

Hetaryl-substituted dienamines (**1a–c** and **4a–c**) of different geometry when treated with dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate (**2**) reacted selectively as enamines (i.e. with the Δ3,4 double bond) to afford the appropriate *E* or *Z* (hetarylvinyl)pyridazines (i.e. **1a–c** gave **3a–c**, whereas **4a–c** afforded **5a–c**). Study on the analogous transformation of the 1*Z* diene ether (**6a**) revealed that, in apolar solvent, isomerization of the olefinic side chain occurred (**3a** rather than **5a** was obtained). Formation of the *trans* product **3a** was rationalized by a tautomeric equilibrium of the supposed intermediate **7** for which experimental evidence was provided.

Earlier, we reported that azolylbutadienes can easily be synthesized by nucleophilic ring opening of fused tetrazolium salts.[1,2] It was also found that these dienes readily undergo cycloadditions both as activated dienes[3] (with electron deficient dienophiles) and as 2π systems[4] (with dipolar 4π or 8π systems, e.g. with tosyl azide and benzofuroxane).

As a continuation of these studies, we decided to investigate the reactivity of such azolylbutadienes toward dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate (**2**). The analogous transformation of electron rich olefins is well-documented in the literature and is a general route to pyridazines.[5] For this purpose, synthesis of a series of azolyl dienamines having different diene geometries[6] (i.e. 1*E* (**1a–c**) and 1*Z* (**4a–c**)) seemed desirable.

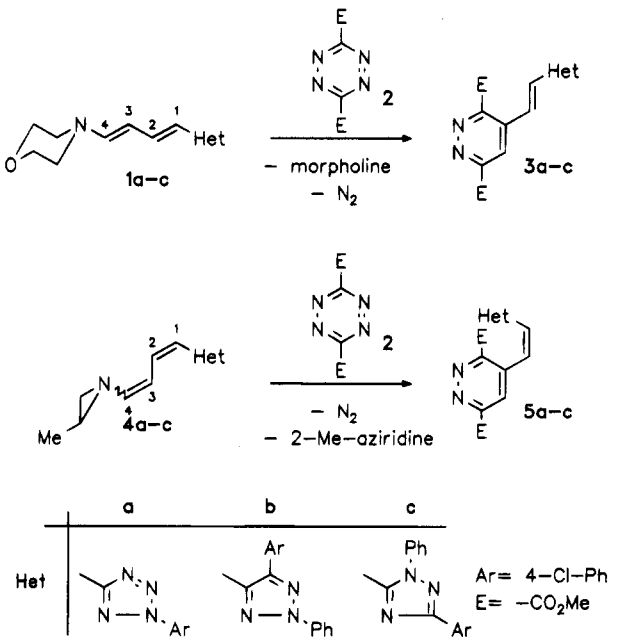
It was found that the *all-trans* dienamines **1a–c** readily reacted with the tetrazine reagent **2** under mild conditions and afforded crystalline products in acceptable (60%) yields. Spectral analysis of the products revealed that the $\Delta^{3,4}$ double bond of the starting dienes took part in these cycloadditions, whereas the $\Delta^{1,2}$ double bond preserved its *E* geometry and, thus, *E* (azolylvinyl)-pyridazine diesters **3a–c** were formed (Scheme 1).

The 2-methylaziridinyl dienes (**4a–c**) which can only be obtained as mixtures of 1*Z*,3*Z* and 1*Z*,3*E* isomers also underwent similar reactions and as expected yielded the *Z* products **5a–c** in which, accordingly, the olefinic side chain proved to be of *Z* geometry.

These successful transformations prompted us to extend this study to the cyclization with tetrazolyl diene ethers, too. These compounds can only be prepared[1,2] in the isomeric forms having a 1*Z* double bond (i.e. **6a** was obtained as a mixture of 1*Z*,3*Z* and 1*Z*,3*E* isomers). It was found that diene ether **6a** also reacted with the tetrazine reagent **2** and afforded unexpectedly two different products depending on the solvent used: *Z* (tetrazolylvinyl)pyridazine diester **5a** was obtained when the reaction was carried out in acetonitrile at room temperature, whereas the *E* isomer **3a** was isolated when the reactants were refluxed in toluene for several hours. The finding that the olefinic side chain underwent isomerization in toluene seemed of particular interest as our previous efforts to isomerize the starting 1*Z* diene **6a** to a 1*E* isomer under the conditions used in these conversions were unsuccessful. Isomerization of the *Z* reaction product **5a** to **3a** was also ruled out by the following experiment: **5a** was refluxed in toluene for 24 h, whereupon only the starting compound was recovered besides some decomposition impurities.

The lack of isomerization of both the starting diene **6a** and the *cis* end product **5a** suggested that the observed isomerization process has to take place on the intermediate **7**. Such dihydropyridazine intermediates are generally not stable and easily undergo elimination or oxidation to give the rearomatized pyridazines; hence, only very little is known of their structure.[7] Moreover, the

Scheme 1



[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

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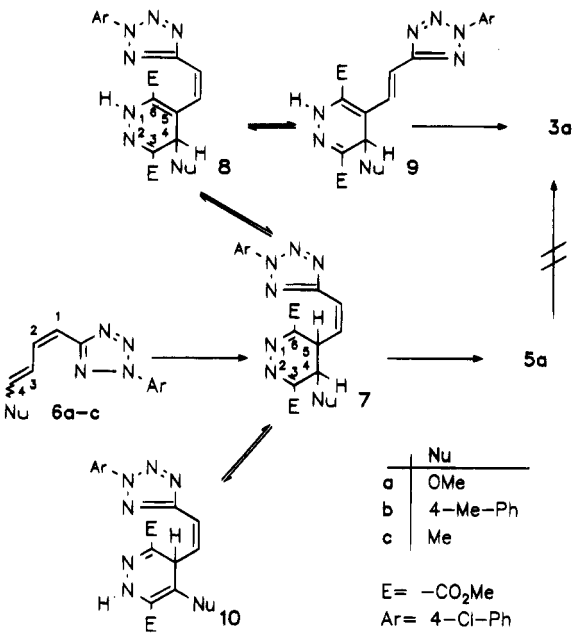
(5) For the synthesis and application of **2**, see: (a) Boger, D. L.; Coleman, R. S.; Panek, J. S.; Huber, F. X.; Sauer, J. *J. Org. Chem.* **1985**, *50*, 5377. (b) Boger, D. L.; Patel, M. *J. Org. Chem.* **1988**, *53*, 1405.

(6) For an explanation of the selective formation of 1*Z* and 1*E* dienes, see ref 2.

(7) Sauer, J. *Acta Chim. Slov.* **1994**, *41*, 235; *Chem. Abstr.* **1995**, *122*, 31355.

0022-3263/95/1960-4919$09.00/0

Scheme 2



particular case of **7** with a vinyl substituent has never been studied before.

In order to check the supposed isomerization of the side chain of **7**, attempts were made to isolate this intermediate by interrupting the cycloaddition. Separation of the reaction mixture by flash chromatography resulted in separation of a new component which was analyzed by ^{1}H NMR. This spectrum revealed that this isolated component was indeed a dihydropyridazine derivative, but the structure **8** (Nu = OCH_3) was formed instead of the expected **7**, which means that a tautomerization on C-5 and N-1 took place (Scheme 2). This tautomer has a dienamine substructure—i.e. N-1, C-6, C-5, and the olefinic part of the molecule—which, through the delocalization of the nitrogen lone pair, can undergo a facile isomerization[8] to the more stable *E* compound **9**, leading to the isolated *E* end product **3a**. The suggested path from **7** to **3a** through tautomers **8** and **9** seemed also to be in agreement with the finding that in acetonitrile, where the final elimination step to **5a** is presumably very fast and hence the lifetime of the intermediates is probably too short to allow for the isomerization, the olefinic chain retains its geometry and the *Z* product **5a** is formed exclusively.

Additional evidence for the tautomeric behavior of the dihydropyridazine intermediate **7** was provided by investigation of the cycloaddition of the tetrazine reagent **2** with the *p*-tolyl- and methyltetrazolyl dienes **6b** and **6c**. In these cases, similar reactivity as above in the Diels–Alder reaction was expected with the essential difference being that the final elimination is strongly hindered by the C substituents (i.e. methyl and *p*-tolyl groups), and thus, relatively stable dihydropyridazines (**7**) may form.

It was found, accordingly, that both dienes **6b** and **6c** reacted with **2** and afforded dihydropyridazines.[9] The ^{1}H NMR investigation of these products revealed that the derivatives **8** and/or **10** were formed; from the reaction of the *p*-tolyl diene **6b** was obtained exclusively the tautomeric form **10** (Nu = *p*-tolyl), whereas the methyl compound **6c** resulted in a 1:1 mixture of isomers **8** and **10** (Nu = Me). The exclusive formation of the tautomer **10** in the *p*-tolyl compound may well be due to the favorable conjugation of the double bond with the aromatic ring. Thus, by detection of the presence of **8** (Nu = Me), experimental support has been provided for the tautomerism of **7** to **8** which was found to be the key step of the isomerization path from **6a** to **3a**. Our attempts to observe the isomerization of **8** (Nu = Me) to **9** (Nu = Me), unfortunately, failed as the mixture of **8** and **10** rapidly decomposed upon prolonged heating (see also ref 9).

These results show that (i) cycloaddition of azolyl dienes provides a direct route to hitherto unknown *Z* and *E* azolylvinyl-substituted pyridazines and (ii) the tautomeric conditions of the primarily formed dihydropyridazine intermediate can account for the isomerization of the olefinic side chain of these products, the recognition of which can result in elaboration of stereoselective procedures to related compounds.

Experimental Section[10]

Synthesis of the New 1*E* and 1*Z* Butadienes 1b–c and 4b–c. The dienamines were prepared according to the procedure published in ref 2.

4-(4-Chlorophenyl)-5-[4-(morpholin-1-yl)buta-(1*E*,3*E*)-1,3-dienyl]-2-phenyl-2*H*-[1,2,3]triazole (1b): yield 62%; mp 125–127 °C (acetonitrile); UV (MeOH) 280, 326 nm; IR 1620, 1594, 1498, 1020, 963 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 9.0 Hz, 2H), 7.68 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 9.0 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.31 (t, J = 8.5 Hz, 1H), 7.15 (dd, J = 15.0, 11.0 Hz, 1H), 6.35 (d, J = 13 Hz, 1H), 6.23 (d, J = 15.0 Hz, 1H), 5.38 (dd, J = 13.0, 11.0 Hz, 1H), 3.72 (t, J = 4.5 Hz, 4H), 3.04 (t, J = 4.5 Hz, 4H). Anal. Calcd for $C_{22}H_{21}N_4OCl$: C, 67.26; H, 5.39; N, 14.26. Found: C, 67.36; H, 5.47; N, 14.25.

3-(4-Chlorophenyl)-5-[4-(morpholin-1-yl)buta-(1*E*,3*E*)-1,3-dienyl]-1-phenyl-1*H*-[1,2,4]triazole (1c): yield: 71%; mp 152–154 °C (EtOH/H_2O); UV (MeOH) 282, 346 nm; IR 1629, 1596, 1497, 1228, 1117 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 9.0 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 7.49 (dd, J = 15.0, 11.0 Hz, 1H), 7.47 (t, J = 8.5 Hz, 1H), 7.43 (d, J = 9.0 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 6.51 (d, J = 13.0 Hz, 1H), 6.00 (d, J = 15.0 Hz, 1H), 5.30 (dd, J = 13.0, 11.0 Hz, 1H), 3.71 (t, J = 4.5 Hz, 4H), 3.09 (t, J = 4.5 Hz, 4H). Anal. Calcd for $C_{22}H_{21}N_4OCl$: C, 67.26; H, 5.39; N, 14.26. Found: C, 67.22; H, 5.42; N, 14.20.

4-(4-Chlorophenyl)-5-[4-(2-methylaziridin-1-yl)buta-1,3-dienyl]-2-phenyl-2*H*-[1,2,3]triazole (4b): a 45:55 mixture of 1*Z*,3*Z* and 1*Z*,3*E* isomers; yield 56%; ^{1}H NMR (400 MHz, $CDCl_3$) for **4b*ZZ*** δ 8.09 (d, J = 9.0 Hz, 2H), 7.45–7.31 (m, 7H), 6.88 (dd, J = 12.5, 11.5 Hz, 1H), 6.76 (dd, J = 12.5, 8.0 Hz, 1H), 6.17 (d, J = 11.5 Hz, 1H), 6.09 (d, J = 8.0 Hz, 1H), 2.08 (m, 1H), 1.97 (d, J = 6.0 Hz, 1H), 1.85 (d, J = 1.5 Hz, 1H), 1.23 (d, J = 5.5 Hz, 3H); ^{1}H NMR (400 MHz, $CDCl_3$) for **4b*ZE*** δ 8.09 (d, J = 9.0 Hz, 2H), 7.45–7.31 (m, 7H), 6.84 (dd, J = 13.2, 11.5 Hz, 1H), 6.58 (d, J = 13.2 Hz, 1H), 6.29 (dd, J = 11.6, 11.5 Hz, 1H), 6.02 (d, J = 11.6 Hz, 1H), 2.08 (m, 1H), 1.97 (d, J = 6.0 Hz, 1H), 1.85 (d, J = 1.5 Hz, 1H), 1.23 (d, J = 5.5 Hz, 3H). Anal. Calcd for $C_{21}H_{19}N_4Cl$: C, 69.51; H, 5.28; N, 15.44. Found: C, 69.40; H, 5.35; N, 15.60.

3-(4-Chlorophenyl)-5-[4-(2-methylaziridin-1-yl)buta-1,3-dienyl]-1-phenyl-1*H*-[1,2,4]triazole (4c): a 65:35 mixture of 1*Z*,3*Z* and 1*Z*,3*E* isomers; yield 65%; ^{1}H NMR (400 MHz, $CDCl_3$) for **4c*ZZ*** δ 8.05 (d, J = 9.0 Hz, 2H), 7.56 (d, J =

(8) The same mechanism is thought to be responsible for the formation of the 1*E*,3*E* dienamines. See ref 2.

(9) In order to achieve better separation, we stopped the reactions after 45 min when, as monitored by TLC, only the dihydropyridazine was present besides the starting materials. Elongated reaction times led to multicomponent reaction mixtures and decomposition products.

(10) Melting points were measured in open capillary tubes and are uncorrected. The IR spectra were recorded as KBr disks. The NMR spectra were registered using TMS as internal standard.

9.0 Hz, 2H), 7.38–7.20 (m, 5H), 7.12 (dd, J = 11.5, 12.5 Hz, 1H), 6.92 (dd, J = 12.5, 8.0 Hz, 1H), 6.23 (d, J = 8.0 Hz, 1H), 5.96 (d, J = 11.5 Hz, 1H), 2.04 (m, 1H), 1.92 (d, J = 6.0 Hz, 1H), 1.85 (d, J = 1.5 Hz, 1H), 1.22 (d, J = 5.5 Hz, 3H); ^{1}H NMR (400 MHz, $CDCl_3$) for **4c*ZE*** δ 8.05 (d, J = 9.0 Hz, 2H), 7.56 (d, J = 9.0 Hz, 2H), 7.38–7.20 (m, 5H), 7.12 (dd, J = 13.0, 11.5 Hz, 1H), 6.67 (d, J = 13.0 Hz, 1H), 6.34 (dd, J = 11.8, 11.5 Hz, 1H), 5.79 (d, J = 11.8 Hz, 1H), 2.04 (m, 1H), 1.92 (d, J = 6.0 Hz, 1H), 1.85 (d, J = 1.5 Hz, 1H), 1.22 (d, J = 5.5 Hz, 3H). Anal. Calcd for $C_{21}H_{19}N_4Cl$: C, 69.51; H, 5.28; N, 15.44. Found: C, 69.47; H, 5.16; N, 15.36.

Reaction of the Dienamines (1a–c and 4a–c) with Dimethyl 1,2,4,5-Tetrazine-3,6-dicarboxylate (2). To a solution of 1 mmol of the tetrazine reagent (**2**) in 3 mL of acetonitrile was added in portions 1 mmol of the appropriate dienamine, and the resulting dark brown mixture was stirred for 3 h. The precipitated crude pyridazine compound was filtered off and recrystallized from toluene.

4-{(*E*)-2-[2-(4-Chlorophenyl)-2*H*-tetrazol-5-yl]vinyl}-pyridazine-3,6-dicarboxylic acid dimethyl ester (3a): yield 52%; mp 188–192 °C (toluene); UV (MeOH) 304 nm; IR 1750, 1722, 1259, 1137, 999, 978 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.35 (d, J = 16.0 Hz, 1H), 8.13 (d, J = 9.0 Hz, 2H), 7.59 (d, J = 16.0 Hz, 1H), 7.56 (d, J = 9.0 Hz, 2H), 4.15 (s, 3H), 4.12 (s, 3H). Anal. Calcd for $C_{17}H_{13}N_6O_4Cl$: C, 50.94; H, 3.38; N, 20.97. Found: C, 50.90; H, 3.38; N, 20.79.

4-{(*E*)-2-[5-(4-Chlorophenyl)-2-phenyl-2*H*-[1,2,3]triazol-4-yl]vinyl}pyridazine-3,6-dicarboxylic acid dimethyl ester (3b): yield 54%; mp 169–171 °C (toluene); UV (MeOH) 286, 354 nm; IR 1742, 1733, 1257, 1133, 997, 976 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.17 (d, J = 9.0 Hz, 2H), 8.00 (d, J = 15.8 Hz, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.54 (t, J = 8.0 Hz, 2H), 7.53 (d, J = 9.0 Hz, 2H), 7.47 (d, J = 15.8 Hz, 2H), 7.42 (m, 1H), 4.11 (s, 3H), 4.09 (s, 3H). Anal. Calcd for $C_{24}H_{18}N_5O_4Cl$: C, 60.57; H, 3.81; N, 14.72. Found: C, 60.66; H, 3.92; N, 14.57.

4-{(*E*)-2-[5-(4-Chlorophenyl)-2-phenyl-2*H*-[1,2,4]triazol-3-yl]vinyl}pyridazine-3,6-dicarboxylic acid dimethyl ester (3c): yield 48%; mp 245–246 °C (toluene); UV (MeOH) 264, 336 nm; IR 1724, 1575, 1265, 1138, 998, 966 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 16.0 Hz, 1H), 8.27 (s, 1H), 8.22 (d, J = 9.0 Hz, 2H), 7.65–7.43 (m, 7H), 7.18 (d, J = 16.0 Hz, 1H), 4.11 (s, 3H), 4.09 (s, 3H). Anal. Calcd for $C_{24}H_{18}N_5O_4Cl$: C, 60.57; H, 3.81; N, 14.27. Found: C, 60.48; H, 3.83; N, 14.80.

4-{(*Z*)-2-[2-(4-Chlorophenyl)-2*H*-tetrazol-5-yl]vinyl}-pyridazine-3,6-dicarboxylic acid dimethyl ester (5a): yield 32%; mp 170–172 °C (toluene); UV (MeOH) 216, 274 nm; IR 1720, 1271, 1137, 1000, 930 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.90 (d, J = 9.0 Hz, 2H), 7.48 (d, J = 9.0 Hz, 2H), 7.37 (d, J = 12.5 Hz, 1H), 7.11 (d, J = 12.5 Hz, 1H), 4.10 (s, 3H), 4.03 (s, 3H). Anal. Calcd for $C_{17}H_{13}N_6O_4Cl$: C, 50.94; H, 3.27; N, 20.97. Found: C, 50.88; H, 3.40; N, 20.87.

4-{(*Z*)-2-[5-(4-Chlorophenyl)-2-phenyl-2*H*-[1,2,3]triazol-4-yl]vinyl}pyridazine-3,6-dicarboxylic acid dimethyl ester (5b): yield 37%; mp 119–121 °C (toluene); UV (MeOH) 288 nm; IR 1757, 1730, 1279, 1140, 828 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.85 (d, J = 9.0 Hz, 2H), 7.61 (d, J = 8.5 Hz, 2H), 7.45 (dd, J = 8.5, 7.5 Hz, 2H), 7.42 (d, J = 9.0 Hz, 2H), 7.34 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 12.5 Hz, 1H), 6.95 (d, J = 12.5 Hz, 1H), 4.07 (s, 3H), 3.96 (s, 3H). Anal. Calcd for $C_{24}H_{18}N_5O_4Cl$: C, 60.57; H, 3.81; N, 14.72. Found: C, 60.66; H, 3.77; N, 14.68.

4-{(*Z*)-2-[5-(4-Chlorophenyl)-2-phenyl-2*H*-[1,2,4]triazol-3-yl]vinyl}pyridazine-3,6-dicarboxylic acid dimethyl ester (5c): yield 34%; mp 186–188 °C (toluene); UV (MeOH) 260 nm; IR 1735, 1283, 1140, 836 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.87 (d, J = 9.0 Hz, 2H), 7.62–7.53 (m, 5H), 7.35 (d, J = 9.0 Hz, 2H), 7.19 (d, J = 12.5 Hz, 1H), 6.77 (d, J = 12.5 Hz, 1H), 4.11 (s, 3 H), 3.95 (s, 3H). Anal. Calcd for $C_{24}H_{18}N_5O_4Cl$: C, 60.57; H, 3.81; N, 14.72. Found: C, 60.70; H, 3.77; N, 14.59.

Reaction of the Diene Ether 6a with Dimethyl 1,2,4,5-Tetrazine-3,6-dicarboxylate (2). Method A. The reaction was carried out in acetonitrile as described above for the dienamines. Product **5a** was isolated in 52% yield.

Method B. A solution of 1 mmol of the diene ether **6a** and 2 mmol of the tetrazine **2** in 5 mL of toluene was refluxed for 5 h, and then the solvent was removed in vacuo. The residue was triturated with ether, filtered off, and recrystallized from toluene to yield 0.108 g (27%) of **3a**.

Preparation and Isolation of the Dihydropyridazine compounds (8 and 10). One millimole of the appropriate diene (**6a–c**) and 1 mmol of the tetrazine compound (**2**) were refluxed in 5 mL of toluene for 45 min. After evaporation of the solvent, the components were separated by flash chromatography on a deactivated alumina column using hexane/ethyl acetate (5:1) as eluent.

5-{(*Z*)-2-[5-(4-Chlorophenyl)-2*H*-tetrazol-4-yl]vinyl}-4-methoxy-1,4-dihydropyridazine-3,6-dicarboxylic acid dimethyl ester (8, Nu = methoxy): MS m/e (relative intensity) 432 (M^+, 38), 253 (100); UV (MeOH) 268, 384 nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (br s, 1H), 7.99 (d, J = 9.0 Hz, 2H), 7.48 (d, J = 9.0 Hz, 2H), 7.46 (d, J = 12.5 Hz, 1H), 6.89 (d, J = 12.5 Hz, 1H), 5.65 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.72 (s, 3H).

5-{(*Z*)-2-[5-(4-Chlorophenyl)-2*H*-tetrazol-4-yl]vinyl}-4-(4-methylphenyl)-2,5-dihydropyridazine-3,6-dicarboxylic acid dimethyl ester (10, Nu = *p*-tolyl): MS m/e (relative intensity) 492 (M^+, 30), 299 (100); UV (MeOH) 272, 394 nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (br s, 1H), 7.95 (d, J = 9.0 Hz, 2H), 7.48 (d, J = 9.0 Hz, 2H), 7.18 (d, J = 7.5 Hz, 2H), 6.99 (d, J = 7.5 Hz, 2H), 6.56 (d, J = 11.0 Hz, 1H), 6.11 (d, J = 11.0 Hz, 1H), 5.95 (t, J = 11.0 Hz, 1H), 3.72 (s, 3H), 3.65 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.64, 162.72, 162.33, 138.06, 135.35, 134.96, 134.03, 132.41, 129.75, 129.66, 128.89, 128.45, 128.30, 125.01, 120.89, 119.25, 115.49, 52.49, 52.34, 38.85, 21.15.

4-{(*Z*)-2-[5-(4-Chlorophenyl)-2*H*-tetrazol-4-yl]vinyl}-5-methyl-1,4-dihydropyridazine-3,6-dicarboxylic acid dimethyl ester (10, Nu = methyl) and 4-{(*Z*)-2-[5-(4-chlorophenyl)-2*H*-tetrazol-4-yl]vinyl}-5-methyl-2,5-dihydropyridazine-3,6-dicarboxylic acid dimethyl ester (8, Nu = methyl): a 50:50 mixture; MS m/e (relative intensity) 416 (M^+, 48), 111 (100); UV (MeOH) 278, 368 nm; ^{1}H NMR (400 MHz, $CDCl_3$) for **10** δ 8.51 (br s, 1H), 7.96 (d, J = 9.0 Hz, 2H), 7.49 (d, J = 9.0 Hz, 2H), 6.54 (d, J = 10.5 Hz, 1H), 5.88 (d, J = 10.5 Hz, 1H), 5.81 (t, J = 10.5 Hz, 1H), 3.75 (s, 3H), 3.62 (s, 3H), 2.28 (s, 3H); ^{1}H NMR (400 MHz, $CDCl_3$) for **8** δ 8.67 (br s, 1H), 8.13 (d, J = 9.0 Hz, 2H), 7.57 (d, J = 9.0 Hz, 2H), 7.25 (d, J = 12.5 Hz, 1H), 6.69 (d, J = 12.5 Hz, 1H), 4.01 (q, J = 4.5 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 1.02 (d, J = 4.5 Hz, 3H).

Acknowledgment. This research has been carried out with the financial support of OTKA (T016720). Thanks are due to Dr. Eszter Gács-Baitz for her help in the interpretation of the NMR spectra.

JO950439N