# Synthesis of 1-Substituted [1,2,3]Triazolo[4,5-*d*]pyridazines as Precursors for Novel Tetraazapentalene Derivatives



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A series of 1-substituted 4,5-diformyl-[1,2,3]triazole derivatives were prepared by 1,3-dipolar cycloaddition of aryl azides with acetylene dicarboxaldehyde mono-diethylacetal. The triazoles were readily converted into 1-substituted [1,2,3]triazolo[4,5-*d*]pyridazines in good yields. The 1-(2-nitrophenyl)-[1,2,3]triazolo[4,5-*d*]pyridazine was found to be a useful intermediate for the generation of the novel 5*H*-benzo[1,2,3]triazolo[1',2':1,2]triazolo[4,5-*d*]pyridazin-6-ium inner salt ring system.

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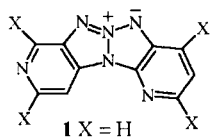
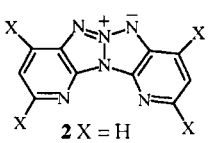
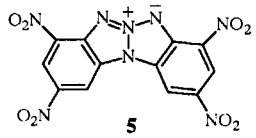
The tetraazapentalene ring system has been the focus of several recent studies aimed at the development of new insensitive energetic materials [1-4]. We recently have reported on the synthesis of 5*H*-pyrido[3",4":4',5'][1,2,3]-triazolo[1',2':2,3][1,2,3]triazolo[5,4-*b*]pyridin-6-ium inner salt (**1**) and 5*H*-pyrido[2",3":4',5'][1,2,3]triazolo[2',1':2,3]-[1,2,3]triazolo[5,4-*b*]pyridin-6-ium inner salt (**2**) [2]. These tetrazaapentalene derivatives were subsequently converted into the tetranitro compounds **3** and **4**, respectively [4]. These novel analogues of the 2,4,8,10-tetranitrobenzotriazolo[1,2-*a*]benzotriazol-6-ium inner salt (**5**, y-Tacot [5]) were found to possess improved energetic properties without significantly increased sensitivity [4]. Based on the performance of **3** and **4**, it became of interest to synthesize tetraazapentalene ring systems with yet higher nitrogen content for the development of new energetic materials. The 5*H*-pyridino[2",3":4',5'][1,2,3]triazolo[1',2':1,2][1,2,3]triazolo[4,5-*d*]pyridazin-6-ium inner salt (**6**) was identified as an attractive synthetic target. As a result of efforts directed toward the synthesis of **6**, we have prepared a series of novel 1-substituted [1,2,3]triazolopyridazines *via* a 1,3-dipolar cycloaddition reaction strategy. Herein, we have prepared a series of novel 1-substituted [1,2,3]triazolopyridazines and related derivatives and we describe their synthesis and structural characterization.



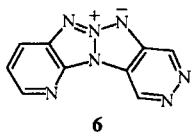
**1** X = H
**3** X = $NO_2$



**2** X = H
**4** X = $NO_2$



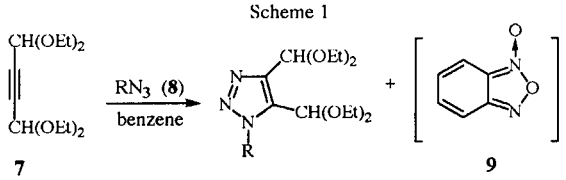
**5**



**6**

There have been several recent reports, which describe the synthesis of trisubstituted-[1,2,3]triazolopyridazines [6-8]. However, there are no general procedures available for the synthesis of 1-substituted [1,2,3]triazolopyridazines. Therefore, it was of interest to develop a general method for the preparation of 1-substituted triazolopyridazines to be employed as intermediates for the construction of tetraazapentalene derivatives. Previous work in this area had demonstrated that acetylene dicarboxaldehyde bis-diethyl acetal (**7**) readily underwent a 1,3-dipolar cycloaddition reaction with phenylazide (**8a**) and benzylazide (**8b**) to afford the corresponding triazoles (Scheme 1) [9]. However, we found that **7** was not

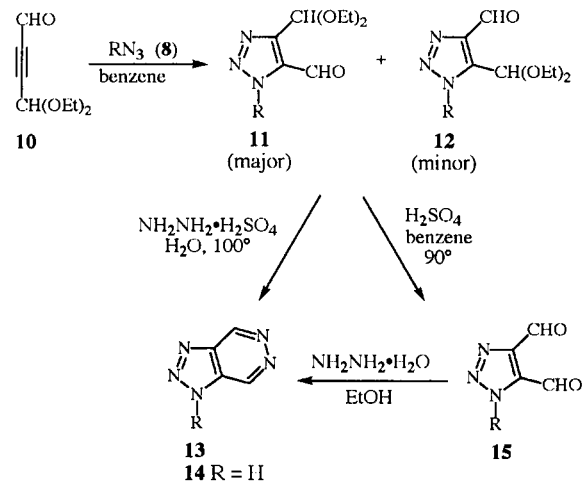
Scheme 1




**7** **9**

sufficiently activated to react as a 1,3-dipolarophile with *ortho*-azidonitrobenzene (**8c**) [10] at low temperature. In fact, it is known that **8c** decomposes to benzofuroxan (**9**) at temperatures of 70-80°[10]. To avoid the thermal decomposition of **8c**, a more reactive 1,3-dipolarophile was required. The acetylene dicarboxaldehyde monodiethylacetal (**10**) [11-13] was prepared and utilized in the 1,3-dipolar cycloaddition reaction with azide **8c**. As illustrated in Scheme 2, the 1,3-dipolar cycloaddition of aryl azide **8c** with **10** in benzene at 55° gave a mixture of two triazole regioisomers **11c** and **12c** (19:1) in 65% yield (Table 1) without formation of the undesired benzofuroxan. The major isomer **11c** could be obtained in pure form by column chromatography.

Scheme 2




R = a) Ph; b) Bn; c) *o*-$NO_2$-Ph; d) *p*-$NO_2$-Ph; e) *o*-$CH_3$-Ph; f) *p*-$CH_3$-Ph.

Table 1
1-Substituted [1,2,3]triazoles **11** and **12**

| analogue | R | **11:12** [a] | Yield (%) [b] |
|---|---|---|---|
| **a** | phenyl | 3:2 | 80 |
| **b** | benzyl | 4:1 | 85 |
| **c** | *o*-$NO_2$-phenyl | 19:1 | 65 |
| **d** | *p*-$NO_2$-phenyl | 3:2 | 82 |
| **e** | *o*-tolyl | 3:1 | 75 |
| **f** | *p*-tolyl | 2:1 | 78 |

[a] Isomer ratios were determined by $^1H$ nmr.
[b] Isolated yields of regioisomer mixtures.

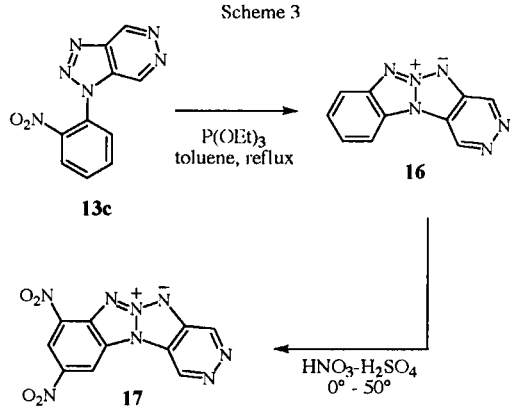
The regioselectivity of the reaction of **8c** was striking since it had been previously reported that the reactions between azides and alkynes generally exhibit poor regioselectivity [14]. This prompted us to further investigate the substituent effects of aryl azides upon the regioselectivity of the 1,3-dipolar cycloaddition reaction with **10**. As shown in Table 1, a series of [1,2,3]triazoles were prepared with yields ranging from 65-85% as mixture of regioisomers **11** and **12**. The structure of each regioisomer was determined by the nmr chemical shift of the acetal methine proton [13]. In the major isomers **11a-f** the methine proton [C*H*$(OEt)_2$] was removed from the shielding region of the aryl ring and had a chemical shift of approximately, δ 6.1 ppm. However, the chemical shift for the methine proton of the minor isomers **12a-f** which lie in closer proximity to the shielding region of the aryl ring was approximately δ 5.9 ppm. A similar trend was observed for the aldehyde proton (C*H*O); however, the shielding effect was not consistent among all of the triazole derivatives.

It is noteworthy that only the *ortho*-nitro group of **8c** had a significant effect upon the regioselectivity of the 1,3-dipolar cycloaddition reaction. The *para*-nitro group of azide **8d** [15] had no effect on regioselectivity and was equivalent to the phenylazide (**8a**) and *para*-tolylazide (**8f**) [16]. A slight regioselective effect was observed for benzylazide (**8b**) and the *ortho*-tolylazide **8e** [16]. Based on these results it is clear that the regioselectivity observed for the reaction of **8c** is due primarily to the electronic effect of the *ortho*-nitro group and to a much lesser extent due to the steric interactions derived from the *ortho*-substitution.

Due to the symmetry of the subsequent pyridazine **13**, the mixture of regioisomers **11** and **12** was routinely carried on to the next reaction (Scheme 2). Conversion of **11/12** into the corresponding pyridazine derivatives **13** was achieved in one step by treatment with hydrazine sulfate in water at 100°. For the conversion of **11c/12c**, along with the expected triazolopyridazine **13c**, [1,2,3]triazolo[4,5-*d*]pyridazine (**14**) was obtained in varying yields *via* loss of the *N*-nitrophenyl group [17]. This side-reaction was overcome by a two-step process which consisted of deprotection of the acetal **11c/12c** with 1*N* sulfuric acid in benzene at 90° using a Dean-Stark apparatus to afford the dialdehyde **15c** in 76% yield. The dialdehyde **15c** was then smoothly converted into the corresponding pyridazine derivative **13c** with ethanolic hydrazine without *N*-dearylation (Scheme 2). This two-step route proved to be general for the conversion of **11a-c** into **13a-c** and provided the 1-substituted triazolopyridizines in good overall yield.

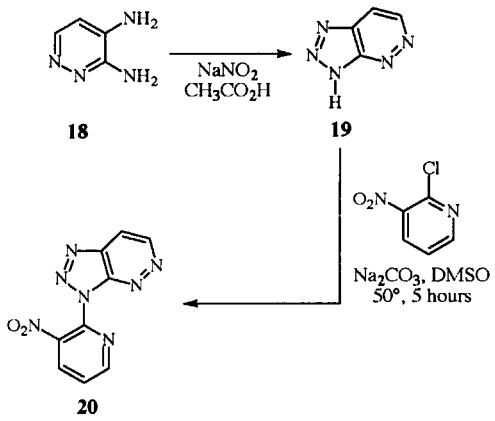
With the 1-(2-nitrophenyl)-[1,2,3]triazolo[4,5-*d*]pyridazine (**13c**) in hand, attention turned toward the construction of the tetrazapentalene ring system. The reductive cyclization of **13c** with triethyl phosphite in toluene at 120° gave **16** in 68% yield (Scheme 3). It was found that toluene was superior to benzene or xylene for this conversion and gave **16** in exceptionally high purity. Subsequent nitration (90% nitric acid/sulfuric acid) of **16** furnished the dinitro compound **17** in 72% yield. It is noteworthy that under these conditions only the benzo ring of **16** was nitrated. Nitration of the pyridazine ring will undoubtedly require more vigorous conditions or alternative nitration reactions.

Scheme 3



The isomer of **14**, [1,2,3]triazolo[4,5-*c*]pyridazine (**19**) [8] was also prepared and evaluated as a precursor for the construction of tetraazapentalene derivatives. As shown in Scheme 4, treatment of 3,4-diaminopyridazine (**18**) [18]

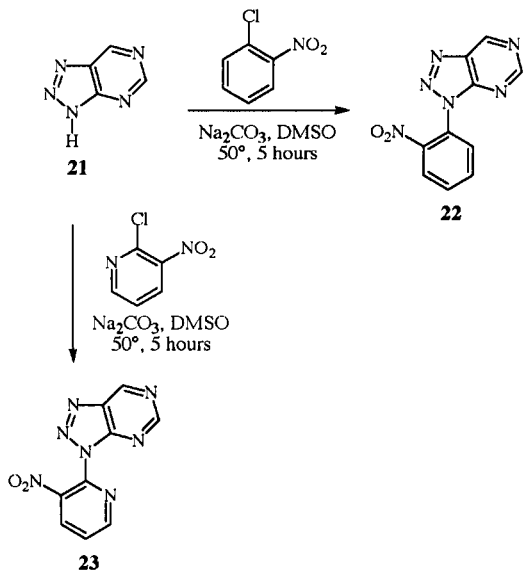
Scheme 4




**18** **19** **20**

in dilute acetic acid with sodium nitrite at 0° afforded **19** in 70% yield. *N*-Arylation of **19** with 2-chloronitrobenzene was unsuccessful; however, *N*-arylation with the more reactive 2-chloro-3-nitropyridine gave 1-(3-nitro-2-pyridyl)-[1,2,3]triazolo[4,5-*c*]pyridazine (**20**) in 45% yield as a single regioisomer. The structure of **20** was unequivocally confirmed by nmr and X-ray crystallographic analysis [19]. In addition, *N*-arylation of [1,2,3]triazolo[4,5-*d*]pyrimidine (**21**) [20] with 2-chloronitrobenzene afforded 1-(2-nitrophenyl)-[1,2,3]triazolo[4,5-*d*]pyrimidine (**22**) in 10% yield (Scheme 5). Likewise, *N*-arylation of **21** with 2-chloro-3-nitropyridine afforded **23** in 60% yield. The structure of **23** was also confirmed by X-ray crystallographic analysis [19]. It is

Scheme 5




**21** **22** **23**

important to note that the *N*-arylation of both **19** and **21** was regiospecific at the 1-position and is consistent with the *N*-arylation chemistry of [1,2,3]triazolopyridines [2]. Unfortunately subsequent reductive cyclization of **20**, **22** and **23** with triethyl phosphite in different solvents (benzene, toluene, xylene) at a variety of reaction temperatures did not give the anticipated tetraazapentalene derivatives and only intractable mixtures were obtained.

## EXPERIMENTAL

All chemicals and reagents not otherwise noted were purchased from Aldrich Chemical Co. The $^1H$ and $^{13}C$ nmr spectra were obtained on Varian-Gemini Multiprobe 400 MHz or Varian-Gemini Multiprobe 300 MHz nmr spectrometers in deuteriochloroform unless otherwise noted. The minor regioisomers **12** were not obtained as pure isomers, hence only characteristic nmr signals are reported. Melting points were determined on a Mel-Temp II and are reported uncorrected. Elemental analyses were obtained from Atlantic Microlab, Inc., Norcross, GA. Caution: Compounds **11c**, **13c**, **17**, **20**, **22** and **23** should be handled as dangerously explosive materials.

General Procedure for the Preparation of 1-Substituted 4-Dimethoxymethyl-5 formyl-[1,2,3]triazoles (**11**) and of 1-Substituted 5-Dimethoxymethyl-4 formyl-[1,2,3]triazoles (**12**).

A solution of aryl azide (**8**) (40 mmol) and acetylene dicarboxaldehyde mono-diethylacetal (**10**) (6.2 g, 40 mmol) in benzene (5 ml) was heated to 90° for 24 hours. The reaction mixture became black and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, hexane: ethyl acetate, 10:1) to afford a mixture of two isomers **9** and **10** in 80-85% combined yield. The minor isomer **12** was not separated from the major isomer, but was carried forth in subsequent reactions.

4-Diethoxymethyl-5-formyl-1-phenyl-[1,2,3]triazole (**11a**).

The mixture **11a/12a** was obtained as colorless oil, 8.8 g (80%). The major isomer **11a** was obtained in pure form as a colorless oil; ir (thin film, sodium chloride) ν 3077, 2967, 2377, 1705, 1608, 1502, 1415 $cm^{-1}$. $^1H$ nmr (300 MHz): δ 10.23 (s, 1H), 7.52 (m, 2H), 7.43 (m, 3H), 5.92 (s, 1H), 3.45 (m, 4H), 1.01 (t, J = 6.95 Hz, 6H); $^{13}C$ nmr: δ 185.1, 143.7, 138.0, 136.0, 129.6, 128.7, 128.5, 127.8, 125.1, 94.3, 63.1, 14.4. **12a** $^1H$ nmr: δ 10.3 (s, 1H), 5.82 (s, 1H).

*Anal.* Calcd. for $C_{14}H_{17}N_3O_3$: C, 61.08; H, 6.22; N, 15.26. Found: C, 61.23; H, 6.04; N, 15.32.

1-Benzyl-4-diethoxymethyl-5-formyl-[1,2,3]triazole (**11b**).

The mixture **11b/12b** was obtained as colorless oil, 9.71 g (84%). The major isomer **11b** was obtained in pure form as a colorless oil; ir (thin film, sodium chloride) ν 3052, 2950, 2332, 1710, 1450, 1400 $cm^{-1}$; $^1H$ nmr (400 MHz): δ 10.20 (s, 1H), 7.34 (m, 5H), 6.15 (s, 1H), 5.75 (s, 2H), 3.73 (m, 4H), 1.13 (t, J = 7Hz, 6H); $^{13}C$ nmr: δ 186.0, 143.2, 137.2, 134.6, 128.6, 128.2, 127.9, 94.1, 63.8, 53.2, 14.6. **12b** $^1H$ nmr: δ 10.15 (s, 1H), 5.89 (s, 1H).

*Anal.* Calcd. for $C_{15}H_{19}N_3O_3$: C, 62.27; H, 6.62; N, 14.52. Found: C, 62.31; H, 6.59; N, 14.38.

4-Diethoxymethyl-5-formyl-1-(2-nitrophenyl)-[1,2,3]triazole (**11c**).

A solution of *o*-azidonitrobenzene **8c** (3.1 g, 19 mmol) and acetylene dicarboxaldehyde mono-diethylacetal (**10**) (2.9 g, 19 mmol) in benzene (3 ml) was heated at 55° for 3 days. This residue was purified by column chromatography (silica gel, hexane:ethyl acetate, 3:1) and furnished the two isomers **11c** and **12c** (19:1) as a white solid, 3.0 g (65%). The major isomer **11c** could be obtained in pure form as a white solid; mp 98-99°; ir (potassium bromide) ν 3114, 2847, 1709, 1608, 1553, 1355, 1207, 1055 $cm^{-1}$. $^1H$ nmr (400 MHz): δ 10.30 (s, 1H), 8.24 (d, J = 8 Hz, 1H), 7.70 (m, 2H), 7.62 (d, J = 7.6 Hz, 1H), 6.07 (s, 1H), 3.52 (m, 4H), 1.01 (t, J = 7.2 Hz, 6H). $^{13}C$ nmr: δ 185.8, 144.8, 143.4, 139.3, 133.6, 131.5, 130.5, 130.3, 125.3, 94.3, 64.0, 14.4. **12c** $^1H$ nmr: δ 10.35 (s, 1H), 5.95 (s, 1H).

*Anal.* Calcd. for $C_{14}H_{16}N_4O_5$: C, 52.50; H, 5.03; N, 17.49. Found: C, 52.40; H, 5.08; N, 17.45.

5-Formyl-4-dimethoxymethyl-1-(4-nitrophenyl)-[1,2,3]triazole (**11d**).

The mixture **11d/12d** was obtained as a solid, 7.95g (82%). The major isomer **11d** was obtained in pure form as a light yellow solid; mp 84-86 °C; ir (potassium bromide) ν 3120, 2798, 1710, 1620, 1550, 1305, 1220, $cm^{-1}$. $^1H$ nmr (300 MHz): δ 10.30 (s, 1H), 8.38 (d, J = 9.6 Hz, 2H), 8.02 (d, J = 8.7 Hz, 2H), 6.24 (s, 1H), 3.62 (m, 4H), 1.05 (t, J = 7.6 Hz, 6H). $^{13}C$ nmr: δ 186.0, 148.1, 144.0, 141.6, 138.2, 126.4, 124.1, 94.4, 64.6, 14.8. **12d** $^1H$ nmr: δ 10.37 (s, 1H), 5.93 (s, 1H).

*Anal.* Calcd. for $C_{14}H_{16}N_4O_5$: C, 52.5; H, 5.03; N, 17.49. Found C, 52.25; H, 5.05; N, 17.40.

1-(2-Methylphenyl)-4-dimethoxymethyl-5-formyl-[1,2,3]triazole (**11e**).

The mixture **11e/12e** was obtained as a colorless oil, 8.67 g (75%). The major isomer **11e** was obtained in pure form as colorless oil; ir (thin film, sodium chloride) ν 2951, 2863, 1709, 1563, 1519, 1431, 1334, 1087 $cm^{-1}$. $^1H$ nmr (400 MHz): δ 10.33 (s, 1H), 7.36 (m, 4H), 5.97 (s, 1H), 3.55 (m, 4H), 2.05 (s, 3H), 1.07 (t, J = 8.4 Hz, 6H). $^{13}C$ nmr: δ 185.2, 143.2, 139.2, 135.2, 130.6, 130.4, 127.1, 126.0, 94.6, 63.5, 17.0, 14.5. **12e** $^1H$ nmr: δ 10.35 (s, 1H), 5.91 (s, 1H).

*Anal.* Calcd. for $C_{15}H_{19}N_3O_3$: C, 62.27; H, 6.62; N, 14.52. Found: C, 62.30; H, 6.52; N, 14.35.

1-(4-Methylphenyl)-4-dimethoxymethyl-5-formyl-[1,2,3]triazole (**11f**).

The mixture **11f/12f** was obtained as a solid, 9.01g (78%). The major isomer **11f** was obtained as a white solid; mp 64-66°C; ir (potassium bromide) ν 2995, 2907, 1704, 1528, 1458, 1369, 1149, 1070 $cm^{-1}$. $^1H$ nmr (300 MHz): δ 10.33 (s, 1H), 7.62 (d, J = 8.7 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 6.02 (s, 1H), 3.55 (m, 4H), 2.44 (s, 3H), 1.11 (t, J = 8.2 Hz, 6H). $^{13}C$ nmr: δ 185.4, 144.0, 140.2, 138.4, 133.9, 129.5, 125.2, 94.7, 63.3, 21.1, 14.7. **12f** $^1H$ nmr: δ 10.29 (s, 1H), 5.95 (s, 1H).

*Anal.* Calcd. for $C_{15}H_{19}N_3O_3$: C, 62.27; H, 6.62; N, 14.52. Found: C, 62.30; H, 6.58; N, 14.60.

General Procedure for the Preparation of 1-Substituted-4,5-diformyl[1,2,3]triazoles (**15**).

A mixture of the mono-diethyl acetals (**11/12**) (4 mmol) in benzene (60 ml) and sulfuric acid (1*N*, 12 ml) was stirred vigorously with azeotropic distillation using a Dean-Stark apparatus. Once all of the water had been removed, the reaction mixture was allowed to cool, the benzene solution was washed with water (2 × 10 ml) and dried over sodium sulfate. The solvent was removed under reduced pressure and chromatographed (silica gel, hexane:ethyl acetate 6:1) to give the dialdehydes **15** in 70-75% yield.

1-Phenyl-4,5 diformyl[1,2,3]triazole (**15a**).

This compound was obtained as a white solid, 0.58 g (72%); mp 104-105° (lit. mp 107° [9]); ir (potassium bromide) ν 3077, 2866, 2232, 1705, 1599, 1548, 1447 $cm^{-1}$; $^1H$ nmr (300 MHz): δ 10.35 (s, 1H), 10.32 (s, 1H), 7.53 (m, 5H). $^{13}C$ nmr: δ 185.4, 179.0, 147.7, 135.2, 133.5, 130.8, 129.2, 125.3.

1-Benzyl-4,5 diformyl[1,2,3]triazole (**15b**).

This compound was obtained as a white solid, 0.65 g (75%) mp 85-86° (lit. mp 89° [9]); ir (potassium bromide) ν 3013, 2865, 1714, 1553, 1507, 1465, 1313 $cm^{-1}$. $^1H$ nmr (300 MHz): δ 10.38 (s, 1H), 10.27 (s, 1H), 7.33 (m, 5H), 5.91 (s, 2H); $^{13}C$ nmr: δ 185.7, 180.2, 147.9, 142.9, 133.5, 132.2, 128.6, 128.2, 54.0.

1-(2-Nitrophenyl)-4,5-diformyl[1,2,3]triazole (**15c**).

This compound was obtained as a light yellow solid, 0.69 g (70%) mp 105-106°; ir (potassium bromide) ν 3050, 2884, 1695, 1613, 1521, 1438, 1387, 1221 $cm^{-1}$. $^1H$ nmr (300 MHz): δ 10.39 (s, 1H), 10.36 (s, 1H), 8.34 (d, J = 7.8 Hz, 1H), 7.86 (m, 2H), 7.54 (d, J = 7.3 Hz, 1H). $^{13}C$ nmr: δ 185.5, 179.3, 147.2, 143.7, 134.5, 134.4, 132.2, 129.5, 129.4, 125.9.

*Anal.* Calcd. for $C_{10}H_6N_4O_4$: C, 48.79; H, 2.46; N, 22.76. Found: C, 48.94; H, 2.55; N, 22.83.

General Procedure for the Preparation of 1-Substituted-[1,2,3]triazolo[4,5-*d*]pyridazines (**13**).

Hydrazine monohydrate (0.50 ml,10 mmol) in absolute ethanol (5 ml) was added dropwise to a stirred solution of the dialdehyde **15** (5 mmol) in absolute ethanol (25 ml) at room temperature. The resulting light yellow solution was heated to 45-50° for 30 minutes. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, chloroform) to give **13** in 80-85% yield.

1-Phenyl-[1,2,3]triazolo[4,5-*d*]pyridazine (**13a**).

This compound was obtained as a white solid, 0.81 g (82%) mp 188-190°; ir (potassium bromide) ν 3022, 2884, 2377, 1737, 1580, 1502, 1281 $cm^{-1}$; $^1H$ nmr (300 MHz): δ 10.02 (s, 1H), 9.86 (s, 1H), 7.70 (m, 5H); $^{13}C$ nmr: δ 142.9, 139.9, 137.1, 133.3, 128.3, 127.9, 127.1, 120.9.

*Anal.* Calcd. for $C_{10}H_7N_5$: C, 60.91; H, 3.58; N, 35.51. Found: C, 60.66; H, 3.64; N, 35.50.

1-Benzyl-[1,2,3]triazolo[4,5-*d*]pyridazine (**13b**).

This compound was obtained as a white solid, 0.89 g (84%) mp 135-136°; ir (potassium bromide) ν 3068, 1580, 1502, 1369, 1304, 1207 $cm^{-1}$. $^1H$ NMR (400 MHz): δ 9.93 (s, 1H), 9.43 (s, 1H), 7.41 (m, 5H), 6.04 (s, 2H); $^{13}C$ nmr: δ 144.8, 142.1, 137.5, 132.5, 129.3, 128.0, 53.5.

*Anal.* Calcd. for $C_{11}H_9N_5$: C, 62.55; H, 4.29; N, 33.16. Found: C, 62.46; H, 4.19; N, 33.29.

1-(2-Nitrophenyl)-[1,2,3]triazolo[4,5-*d*]pyridazine (**13c**).

Hydrazine monohydrate (0.35 ml, 7.3 mmol) in absolute ethanol (10 ml) was added dropwise over 20 minutes to a stirred solution of the dialdehyde **15c** (1.0 g, 4.06 mmol) in absolute ethanol (60 ml) at -5°. The resulting light yellow precipitate was collected by filtration and the solid was purified by column chromatography (silica gel, chloform:acetone, 12:1) to furnish **13c** as a yellow solid, 0.75 g (76% yield); mp 155-156°; ir (potassium bromide) ν 3059, 1613, 1580, 1530, 1350, 1184, 1060 $cm^1$; $^1H$ nmr (400 MHz): δ 10.04 (s, 1H), 9.60 (s, 1H), 8.30 (d, J = 8.4 Hz, 1H), 7.97 (m, 2H), 7.75 (d, J = 7.6 Hz, 1H). $^{13}C$ nmr (deuteriodimethylsulfoxide): δ 142.2, 141.6, 138.6, 136.1, 132.8, 130.0, 128.0, 126.7, 124.5, 123.8.

*Anal.* Calcd. for $C_{10}H_6N_6O_2$: C, 49.59; H, 2.5; N, 34.7. Found: C, 49.34; H, 2.67; N, 34.43.

5*H*-Benzo[1,2,3]triazolo[1',2':1',2'][1,2,3]triazolo[4,5-*d*]pyridazin-6-ium Inner Salt (**16**).

Under a nitrogen atmosphere a solution of triethyl phosphite (2.4 ml, 20 mmol), in toluene (10 ml) was added dropwise to a refluxing solution of **13c** (0.50 g, 2.1 mmol) in toluene (30 ml). The resulting solution was heated to reflux for 6 hours. The solvent and volatile products were removed under reduced pressure. The residue was purified by column chromatography (silica gel, benzene:acetone, 7:1) to yield **16** as a tan solid, 0.32 g (68%); mp 294-295°; ir (potassium bromide) ν 3100, 1510, 1455, 1379, 1328, 1263, 1152, 768 $cm^{-1}$. $^1H$ nmr (300 MHz, deuteriodimethylsulfoxide): δ 10.38 (s, 1H), 9.86 (s, 1H), 8.66 (d, J = 9Hz, 1H), 8.06 (d, J = 7.5 Hz, 1H), 7.71 (m, 2H). $^{13}C$ nmr (deuteriodimethylsulfoxide): δ 140.9, 138.1, 137.2, 132.5, 124.6, 121.6, 119.1, 116.5, 114.2, 109.1.

*Anal.* Calcd. for $C_{10}H_6N_6$: C, 57.14; H, 2.88; N, 39.98. Found: C, 57.25; H, 2.91; N, 39.76.

8,10-Dinitro-5*H*-benzo[1,2,3]triazolo[1',2':1,2]triazolo[4,5-*d*]-pyridazin-6-ium Inner Salt (**17**).

Nitric acid (90%, 4.5 ml) was added dropwise to a stirred solution of **16** (0.18 g, 0.80 mmol) in concentrated sulfuric acid (3 ml) at 0° and the mixture was stirred for 1 hour, then at 50° for 2 hours. The resulting yellow solution was cooled to room temperature and poured into ice-water. The resulting yellow solid was filtered and dried to furnish **17**, 0.18 g (72%); mp 330-332° (expl); ir (potassium bromide) ν 3040, 1625, 1595, 1537, 1472, 1378, 1331, 1278 $cm^{-1}$. $^1H$ nmr (300 MHz, deuterioacetone) δ 10.83 (s, 1H), 10.10 (s, 1H), 10.06 (s, 1H), 9.38 (s, 1H).

*Anal.* Calcd. for $C_{10}H_4N_8O_4$: C, 40.01; H, 1.34; N, 37.33. Found: C, 40.18; H, 1.29; N, 37.24.

[1,2,3]Triazolo[4,5-*c*]pyridazine (**19**).

3,4-Diaminopyridazine **18** (2.5 g, 23 mmol) was dissolved in 10% acetic acid (150 ml) and cooled to 0-5°. To this mixture a solution of sodium nitrite (3.1 g, 45 mmol) in water (37 ml) was added with stirring. The reaction mixture was heated to 80° for 30 minutes and concentrated to obtain a residue. This residue was dissolved in water (20 ml) acidified with 10% hydrochloric acid to give tan solid. This solid was filtered, washed with cold water and under vacuum dried to afford **19**, 1.9 g (78%); mp 226-227° (lit. mp 227-228° [8]); $^1H$ nmr (deuteriodimethylsulfoxide): δ 8.35 (d, J = 6.8 Hz, 1H), 9.34 (d, J = 6.8 Hz, 1H).

1-(3-Nitro-2-pyridyl)-[1,2,3]triazolo[4,5-*c*]pyridazine (**20**).

A mixture of [1,2,3]triazolo[4,5-*c*]pyridazine (**19**) (1.2 g, 10 mmol), sodium carbonate (1.6 g, 15 mmol) and 2-chloro-3-nitro-pyridine (1.7 g, 11 mmol) in anhydrous dimethylsufoxide (4 ml) was heated to 50° for 5 hours. The brown mixture was cooled to room temperature and poured into water (15 ml). The precipitate was filtered, dried under vacuum and purified by column chromatography (silica gel, benzene:acetone, 25:1) to give **20**, 1.1 g (45%); mp 160-162° (expl); ir (potassium bromide) ν 3119, 3036, 1607, 1542, 1460, 1366, 1331, 1155, 1067 $cm^{-1}$. $^1H$ nmr (400 MHz) δ 9.50 (d, J = 6 Hz, 1H), 8.87 (dd, J = 1.6, 4.8 Hz, 1H), 8.44 (dd, J = 1.6, 8.4 Hz, 1H), 8.32 (d, J = 6 Hz, 1H), 7.71 (q, J = 4.8, 8.0 Hz, 1H). $^{13}C$ nmr (deuteriodimethylsulfoxide): δ 159.3, 150.1, 145.9, 136.8, 136.6, 133.4, 123.3, 121.9, 108.6.

*Anal.* Calcd. for $C_9H_5N_7O_2$: C, 44.45; H, 2.07; N, 40.25. Found: C, 44.51; H, 1.97; N, 40.41.

1-(2-Nitrophenyl)-[1,2,3]triazolo[4,5-*d*]pyrimidine (**22**).

A mixture of [1,2,3]triazolo[4,5-*d*]pyrimidine (**21**) (0.60 g, 0.5 mmol), sodium carbonate (0.79 g, 7.5 mmol) and 2-chloronitrobenzene(0.86 g, 5.5 mmol) in anhydrous dimethylsulfoxide (3 ml) was heated to 95° for 12 hours. The brown mixture was cooled to room temperature and poured into water (8 ml). The precipitate was filtered, dried under vacuum and purified by column chromatography (silica gel, chloroform:methanol, 50:1) to give **22**, 0.12 g (10%); 159-160° ir (potassium bromide) ν 3112, 3050, 1248, 1525, 1440, 1325, 1180 $cm^{-1}$. $^1H$ nmr (300 MHz) δ 9.41 (s, 1H), 9.20 (s, 1H), 8.3, (dd, J = 1.5, 8.1 Hz, 1H), 7.9 (m, 2H), 7.72 (dd, J = 1.5, 7.8 Hz, 1H).

*Anal.* Calcd. for $C_{10}H_6N_6O_2$: C, 49.59; H, 2.5; N, 34.7. Found: C, 49.72; H, 2.36; N, 34.82.

1-(3-Nitro-2-pyridyl)-[1,2,3]triazolo[4,5-*d*] pyrimidine (**23**).

A mixture of [1,2,3]triazolo[4,5-*d*]pyrimidine (**21**) (1.2 g, 10 mmol), sodium carbonate (1.6 g, 15 mmol) and 2-chloro-3-nitro-pyridine (1.7 g, 11 mmol) in anhydrous dimethylsufoxide (4 ml) was heated to 50° for 5 hours. The brown mixture was cooled to room temperature and poured into water (15 ml). The precipitate was filtered, dried under vacuum and purified by column chromatography (silica gel, benzene:acetone, 25:2) to give **23**, 1.5 g (60%); mp 164-165° (expl); ir (potassium bromide) ν 3080, 3060, 1595, 1566, 1466, 1407, 1360, 1313, 1078, 1014 $cm^{-1}$. $^1H$ nmr (300 MHz) δ 10.01 (s, 1H), 9.39 (s, 1H), 9.06 (dd, J = 1.5, 4.8 Hz, 1H), 8.75 (dd, J = 1.5, 8.1 Hz, 1H), 8.0 (g, J = 4.5, 8.1 Hz, 1H) $^{13}C$ nmr (deuteriodimethylsulfoxide): δ 157.2, 152.6, 149.8, 144.4, 136.5, 136.2, 133.2, 123.0, 119.9.

*Anal.* Calcd. for $C_9H_5N_7O_2$: C, 44.45; H, 2.07; N, 40.25. Found: C, 44.52; H, 2.16; N, 40.30.

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