904, 747 cm^{-1}; MS, m/e calcd for $C_{13}H_{17}NOS$ (M^+) 235.1031, obsd 235.1032.

***trans*-4,5-Dihydro-3-(phenylthio)-4,5-dipropylisoxazole (6d)**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (2 H, m), 7.35 (3 H, m), 4.29 (1 H, m), 2.80 (1 H, m), 1.7–1.2 (8 H, m), 0.90 (6 H, m); ^{13}C NMR δ 158.4 (s), 133.9 (d), 129.2 (d), 128.7 (d), 85.8 (d), 55.2 (d), 37.3 (t), 33.2 (t), 19.7 (t), 18.5 (t), 13.9 (q), 13.8 (q); IR (thin film) 3050, 2959, 2932, 2872, 1477, 1441, 876, 747 cm^{-1}; MS, m/e calcd for $C_{15}H_{21}NOS$ (M^+) 263.1345, obsd 263.1344.

(3aα,4β,7β,7aα)-3a,4,5,6,7,7a-Hexahydro-4,7-methano-3-(phenylthio)-1,2-benzisoxazole (6e): ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (2 H, m), 7.36 (3 H, m), 4.51 (1 H, d, J = 8.3 Hz), 3.04 (1 H, d, J = 8.3 Hz), 2.53 (1 H, br s), 2.40 (1 H, br s), 1.6–0.9 (6 H, m); IR (thin film) 3050, 2963, 1476, 1441, 1219, 864, 748 cm^{-1}; MS, m/e calcd for $C_{14}H_{15}NOS$ (M^+) 245.0876, obsd 245.0876. Anal. Calcd for ($C_{14}H_{15}NOS$): C, 68.54; H, 6.16. Found: C, 68.60; H, 6.30.

3a,5,6,6a-Tetrahydro-3-(phenylthio)-4*H*-cyclopent[*d*]isoxazole (6f): ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (2 H, m), 7.35 (3 H, m), 5.09 (1 H, m), 3.58 (1 H, br t), 2.06 (2 H, m), 1.66 (4 H, m); ^{13}C NMR δ 157.6 (s), 133.6 (d), 129.4 (d), 128.9 (d), 87.1 (d), 55.2 (d), 36.0 (t), 31.2 (t), 23.2 (t); IR (thin film) 3050, 2959, 1441, 1476, 884, 746, 691 cm^{-1}; MS, m/e calcd for $C_{12}H_{13}NOS$ (M^+) 219.0718, obsd 219.0719.

3a,4,5,6,7,7a-Hexahydro-3-(phenylthio)-1,2-benzisoxazole (6g): ^1H NMR (300 MHz, $CDCl_3$) δ 7.57 (2 H, m), 7.35 (3 H, m), 4.45 (1 H, m), 2.91 (1 H, q), 2.02 (1 H, m), 1.9–1.6 (6 H, m), 1.21 (1 H, m); ^{13}C NMR δ 162.8 (s), 136.7 (d), 129.3 (d), 128.8 (d), 79.6 (d), 47.8 (d), 25.4 (t), 21.8 (t), 20.2 (t); IR (thin film) 3050, 2936, 2861, 1476, 1441, 862, 747 cm^{-1}; MS m/e calcd for $C_{13}H_{15}NOS$ (M^+) 233.0874, obsd 233.0874.

***cis*-4,5-Dihydro-5-isopropyl-4-methyl-3-(phenylthio)isoxazole (6h)**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.6–7.3 (5 H, m), 3.93 (1 H, m), 2.94 (1 H, m), 2.02 (1 H, m), 1.08 (6 H, two overlapping doublets), 0.90 (3 H, d, J = 6.6 Hz); ^{13}C NMR δ 157.9 (s), 133.3 (d), 129.4 (d), 128.9 (d), 90.1 (d), 46.4 (d), 27.3 (d), 19.8 (q), 11.1 (q); MS, m/e calcd for $C_{13}H_{17}NOS$ (M^+) 235.1031, obsd 235.1032.

General Procedure for the Preparation of (Phenylsulfonyl)isoxazolines: 5-Butyl-4,5-dihydro-3-(phenylsulfonyl)isoxazole (2a). *m*-CPBA (176 mg, 1.02 mmol) was added in one portion to a solution of 3-(phenylthio)-5-butyl-Δ^2-isoxazoline **6a** (100 mg, 0.43 mmol) in methylene chloride (5 mL) at 0 °C. After being stirred at room temperature for 1 h, the reaction mixture was diluted with water and poured into a separatory funnel. After extraction with Et_2O (×3) and washing with brine, the mixture was dried over $MgSO_4$ and concentrated. The crude product was purified by flash chromatography to give 111 mg (97%) of **2a**: ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 (2 H, d), 7.72 (1 H, t), 7.61 (2 H, t), 4.84 (1 H, m), 3.36 (1 H, dd, J = 10.7, 17.0 Hz), 2.96 (1 H, dd, J = 8.5, 17.0 Hz), 1.9–1.2 (6 H, m), 0.88 (3 H, t, J = 6.6 Hz); ^{13}C NMR δ 160.0 (s), 137.0 (s), 134.8 (d), 129.5 (d), 128.8 (d), 85.3 (d), 37.4 (t), 34.5 (t), 27.0 (t), 22.3 (t), 13.9 (q); IR (thin film) 3050, 2957, 2934, 1448, 1332, 1167, 1128, 923, 723 cm^{-1}; MS, m/e calcd for $C_9H_8NO_3S$ ($M^+ - C_4H_9$) 210.0225, obsd 210.0224.

4,5-Dihydro-5-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]ethyl]-3-(phenylsulfonyl)isoxazole (2b): ^1H NMR (300 MHz, $CDCl_3$) major (anti) isomer δ 8.0–7.5 (5 H, m), 4.72 (1 H, m), 4.03 (1 H, m), 3.40 (1 H, dd, J = 8.6, 17.0 Hz), 3.24 (1 H, dd, J = 11.4, 17.0 Hz), 1.07 (3 H, d, J = 6.2 Hz), 0.78 (9 H, s), 0.04 (3 H, s), 0.01 (3 H, s); minor (syn) isomer δ 3.91 (1 H, m), 0.84 (9 H, s), –0.07 (6 H, s); IR (thin film) 3050, 2955, 2930, 1335, 1169, 837, 611 cm^{-1}; MS, m/e calcd for $C_{13}H_{18}NO_3SSi$ ($M^+ - C_4H_9$) 312.0721, obsd 312.0722.

4,5-Dihydro-5-methyl-3-(phenylsulfonyl)-5-propylisoxazole (2c): ^1H NMR (300 MHz, $CDCl_3$) δ 8.0–7.55 (5 H, m), 3.16 (1 H, d, J = 17.2 Hz), 2.97 (1 H, d, J = 17.2 Hz), 1.65 (2 H, m), 1.39 (3 H, s), 1.31 (2 H, m), 0.93 (3 H, t); ^{13}C NMR δ 159.0 (s), 137.4 (s), 134.6 (d), 129.4 (d), 128.6 (d), 92.5 (s), 42.1 (t), 25.3 (q), 17.0 (t), 14.0 (q); IR (thin film) 3050, 2963, 2934, 1449, 1330, 1169, 723 cm^{-1}; MS, m/e calcd for $C_{13}H_{17}NO_3S$ (M^+) 267.0929, obsd 267.0929.

***trans*-4,5-Dihydro-3-(phenylsulfonyl)-4,5-dipropylisoxazole (2d)**: ^1H NMR (300 MHz, $CDCl_3$) δ 8.00–7.55 (5 H, m), 4.52 (1 H, m), 3.31 (1 H, m), 2.0–1.2 (8 H, m), 0.94 (3 H, t, J = 7.2 Hz), 0.91 (3 H, t, J = 7.1 Hz); IR (thin film) 3050, 2961, 2934, 2874, 1448, 1327, 1166, 725 cm^{-1}; MS, m/e calcd for $C_{15}H_{21}NO_3S$ (M^+) 295.1242, obsd 295.1242.

(3aα,4β,7β,7aα)-3a,4,5,6,7,7a-Hexahydro-4,7-methano-3-(phenylsulfonyl)-1,2-benzisoxazole (2e): mp 86–87 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.00–7.55 (5 H, m), 4.70 (1 H, d, J = 8.5 Hz), 3.44 (1 H, d, J = 8.5 Hz), 2.77 (1 H, br s), 2.59 (1 H, br s), 1.7–1.0 (6 H, m); IR (thin film) 2966, 1448, 1332, 1166, 1131, 722 cm^{-1}; MS, m/e calcd for $C_{14}H_{15}NO_3S$ (M^+) 277.0772, obsd 277.0772. Anal. Calcd for $C_{14}H_{15}NO_3S$: C, 60.63; H, 5.45. Found: C, 60.71; H, 5.51.

3a,5,6,6a-Tetrahydro-3-(phenylsulfonyl)-4*H*-cyclopent[*d*]isoxazole (2f): ^1H NMR (300 MHz, $CDCl_3$) δ 8.0–7.5 (5 H, m), 5.28 (1 H, m), 4.02 (1 H, br t), 2.33 (1 H, m), 2.16 (1 H, m), 1.76 (3 H, m), 1.47 (1 H, m); IR (thin film) 3050, 2965, 1447, 1327, 1161, 725, 639 cm^{-1}; MS, m/e calcd for $C_{12}H_{13}NO_3S$ (M^+) 251.0616, obsd 251.0615.

3a,4,5,6,7,7a-Hexahydro-3-(phenylsulfonyl)-1,2-benzisoxazole (2g): ^1H NMR (300 MHz, $CDCl_3$) δ 8.05–7.55 (5 H, m), 4.62 (1 H, m), 3.43 (1 H, br q), 2.06 (2 H, m), 1.8–1.2 (6 H, m); IR (thin film) 3050, 2940, 2865, 1447, 1310, 1163, 725 cm^{-1}; MS, m/e calcd for $C_{13}H_{15}NO_3S$ (M^+) 265.0773, obsd 265.0772. Anal. Calcd for $C_{13}H_{15}NO_3S$: C, 58.85; H, 5.70. Found: C, 58.52; H, 5.97.

***cis*-4,5-Dihydro-5-isopropyl-4-methyl-3-(phenylsulfonyl)isoxazole (2h)**: ^1H NMR (300 MHz, $CDCl_3$) δ 8.01–7.55 (5 H, m), 4.10 (1 H, dd, J = 8.5, 9.8 Hz), 3.52 (1 H, m), 2.04 (1 H, m), 1.25 (3 H, d, J = 7.2 Hz), 1.06 (3 H, d, J = 6.4 Hz), 0.95 (3 H, d, J = 6.6 Hz); IR (thin film) 1447, 1329, 1211, 1165, 723 cm^{-1}; MS, m/e calcd for $C_{13}H_{17}NO_3S$ (M^+) 267.0929, obsd 267.0929.

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Registry No. 2a, 70367-25-8; **2b** (isomer 1), 116503-05-0; **2b** (isomer 2), 116503-10-7; **2c**, 116503-06-1; **2d**, 116503-07-2; **2e**, 70367-26-9; **2f**, 108470-81-1; **2g**, 108470-80-0; **2h**, 116503-08-3; **6a**, 116502-97-7; **6b** (isomer 1), 116502-98-8; **6b** (isomer 2), 116503-09-4; **6c**, 116502-99-9; **6d**, 116503-00-5; **6e**, 116503-01-6; **6f**, 116503-02-7; **6g**, 116503-03-8; **6h**, 116503-04-9; H_2C=CHCH(OTBS)CH_3, 90270-45-4; H_2C=C(CH_3)$(CH_2)_2CH_3$, 763-29-1; (*E*)-PrCH=CHPr, 14850-23-8; (*Z*)-H_3CCH=CHCH$(CH_3)_2$, 691-38-3; phenylthionitrile oxide, 77721-72-3; phenylthionitromethane, 60595-16-6; 1-hexene, 592-41-6; norbornene, 498-66-8; cyclopentene, 142-29-0; cyclohexene, 110-83-8.

Tetrazolo[1,5-*b*][1,2,4]triazines: An Alternate Synthesis and Chemistry

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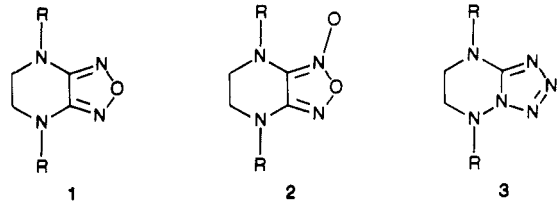
We recently reported on the synthesis and chemistry of some furazano- and furoxano[3,4-*b*]piperazines (**1** and **2**).[1] This paper summarizes some similar work on the related 5,6,7,8-tetrahydrotetrazolo[1,5-*b*][1,2,4]triazines (**3**) in which a tetrazole ring has replaced the furazan or furoxan ring in **1** and **2**. These compounds were of interest be-

(1) Willer, R. L.; Moore, D. W. *J. Org. Chem.* **1985**, *50*, 5123.

0022-3263/88/1953-5371$01.50/0

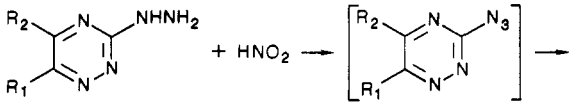


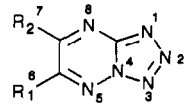
1 2 3

cause, like the furazans and furoxans, calculations[2,3] had predicted that the nitrated derivatives of these would be dense and energetic, and they would be the first examples of 1-nitraminotetrazoles.

Results

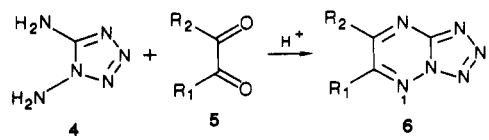
Synthesis. There appeared to be two routes for the synthesis of the desired 5,6,7,8-tetrahydrotetrazolo[1,5-*b*][1,2,4]triazines. The first was to fuse the tetrazole ring onto an existing 1,2,4-triazine or tetrahydro 1,2,4-triazine ring, and the second was to fuse the 1,2,4-triazine ring onto a preformed tetrazole ring followed by reduction. Tetrazolo[1,5-*b*][1,2,4]triazenes have already been synthesized by Paudler et al.[4] by the treatment of the appropriate 3-hydrazino-1,2,4-triazines[5] with nitrous acid as shown below. This generates 3-azido-1,2,4-triazines, which cyclize





yield, %	compound
33	**6a**: $R_1 = R_2 = H$
82	**b**: $R_1 = CH_3$; $R_2 = H$
50	**c**: $R_1 = H$; $R_2 = CH_3$
70	**d**: $R_1 = R_2 = CH_3$

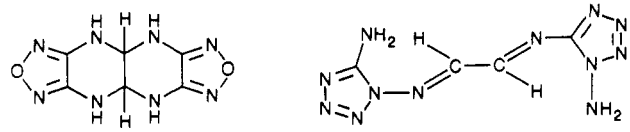
to the desired tetrazolo[1,5-*b*][1,2,4]triazines. However, the yields for this reaction are not high, and the synthesis of the required 3-hydrazino-1,2,4-triazines is a multistep synthesis involving unpleasant sulfur compounds. We therefore chose to examine an alternate synthesis of the tetrazolo[1,5-*b*][1,2,4]triazines based on the reaction of 1,5-diaminotetrazole (DAT) with glyoxals. This route was attractive because of the ready availability of DAT from a new one-step reaction.[6] Reaction of DAT with 1 equiv of glyoxal, pyruvic aldehyde, or biacetyl in water with an acid catalyst yielded the desired tetrazolo[1,5-*b*][1,2,4]-triazines (**6a–d**) contaminated in the glyoxal and pyruvic aldehyde cases with a small amount of a highly insoluble byproduct. The reactions are summarized in Table I in



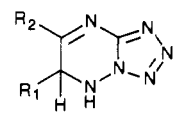
4 5 6

the Experimental Section. The product from pyruvic aldehyde is an inseparable 50/50 mixture of the two possible (6-methyl and 7-methyl) isomeric products. An authentic sample of **6c** was prepared by the Paudler procedure. On the basis of our experience with the Paudler method, the DAT condensation method is superior for the synthesis of any tetrazolo[1,5-*b*][1,2,4]triazines in which the 6- and 7-positions are alike.

The insoluble byproducts in the reaction of DAT and glyoxal and pyruvic aldehyde appeared to be 2:1 condensation products similar to that obtained previously from diaminofurazan and glyoxal (i.e., **7**).[1] Changing the reaction stoichiometry to 2:1 gave these as the major product for glyoxal and pyruvic aldehyde but not with biacetyl. However, instead of the tetracyclo compound **7** obtained in the 3,4-diaminofurazan case, these products appear to be diimines. In the glyoxal case, the methine protons appear as an AB quartet centered at δ 8.25 (J = 9 Hz), while in **7** the methine protons appear as a singlet at 5.02 ppm. These data are consistent with the unsymmetrical isomer **8**. In the pyruvic aldehyde case the product is a 3:1 mixture of two isomers. Also, reaction of **6a** with DAT gives **8**, which suggests that the condensations are reversible.

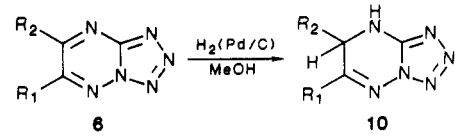


7 8



9

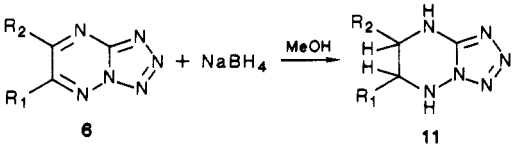
Reduction. Initial attempts to reduce the tetrazolo-[1,5-*b*][1,2,4]triazines by hydrogenation with a Pd/C catalyst consistently stopped after the absorption of 1 mol of hydrogen. From the reactions with **6a** and **6d**, compounds were isolated whose spectral data were consistent with either a 5,6-dihydro (**9**) or 7,8-dihydro structure (**10**). Structure **10** for these products was established by synthesizing an authentic sample of 7-methyltetrazolo[1,5-*b*][1,2,4]triazine (**6c**) by the method of Paudler and reducing this compound with use of the same conditions as were used for the reduction of **6a** and **6d**. Isolated from this reaction was a compound whose structure was clearly **10c** because the methyl group appeared as a doublet (J = 6.0 Hz) in the ^{1}H NMR spectrum. Data for these compounds are summarized in Table II in the Experimental Section.



6 10

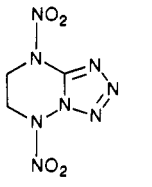
We next examined the reduction of the tetrazolo[1,5-*b*][1,2,4]triazines with sodium borohydride in methanol since previous work had shown that this reagent reduces the related tetrazolo[1,5-*b*]pyridazines to 5,6,7,8-tetrahydrotetrazolo[1,5-*b*]pyridazines.[7] Compounds **6a–d** are rapidly reduced with sodium borohydride in methanol to give high yields of the 5,6,7,8-tetrahydro compounds **11a–e**. Data for these compounds are summarized in Table III in the Experimental Section. Reduction of the mixture of

(2) Cichra, D. A.; Holden, J. R.; Dickinson, C. NSWC Report TR799-273 (Naval Surface Weapons Center, Silver Spring, MD, 1980), p 39.
(3) (a) Rothstein, L. R.; Petersen, R. *Prop. Explos.* **1979**, *4*, 56–60 (b) Rothstein, L. R. *Prop. Explos.* **1981**, *6*, 91–93.
(4) Goodman, M. M.; Atwood, J. L.; Carlin, R.; Hunter, W.; Paudler, W. W. *J. Org. Chem.* **1976**, *41*, 2860.
(5) Paudler, W. W.; Chen, T. K. *J. Heterocycl. Chem.* **1970**, *7*, 767.
(6) Gaponik, P. N.; Karavai, V. P. *Khim Getero. Soed. (Engl. Transl.)* **1984**, 1683.
(7) Kadaba, P. K.; Stanovnik, B.; Tisler, M. *J. Heterocycl. Chem.* **1976**, *13*, 835.



6b and **6c** gives, as expected, a mixture of two positional isomers (i.e., 6-methyl **11b** and 7-methyl **11c**). One compound crystallized from the mixture of **11b** and **11c**. This compound was shown to be the 6-methyl isomer, **11b**, by X-ray crystallography.[8] The 7-methyl isomer, **11c**, was obtained pure by reduction of a sample of **6c** prepared via the azide. Reduction of **6d** gives a mixture of two stereoisomer (i.e., cis and trans). The mixture could be easily separated by fractional crystallization from water. The less soluble, minor isomer, **11e**, was assigned the trans structure on the basis of its lower solubility and the magnitude of the coupling constant between N_5H and C_6H. The crystal structure of **11b** showed the methyl group on C_6 is in a pseudoequatorial position (C_6H axial!) and N_5H is axial. There is a 10-Hz coupling between N_5H and C_6H in **11b**. The less soluble isomer from the reduction of **6d** also has a 10-Hz coupling and thus should have a similar relation between N_5H and C_6H. This is only possible in the trans isomer since the cis isomer would be expected to be undergoing a rapid interconversion between two nearly equal energy conformations. The rapid reduction of **6a–d** is in line with the previous observations of Kadaba, Stanovnik, and Tisler[7] on the rate of reduction of imidazo[1,2-*b*]-, -s-triazolo[4,3-*b*]-, and tetrazolo[1,5-*b*]-pyridazines where the compounds with greater numbers of nitrogen atoms are reduced more rapidly with sodium borohydride.

Nitrations. The nitro derivatives of **10a** and **11a** were of interest in connection with our general study of high-energy nitramines. Nitration of **11a** proceeded smoothly in acetic anhydride/nitric acid to give the 5,8-dinitro compound **12**. This is the first example of a 1-nitraminotetrazole synthesized, and the compound has six nitrogen atoms contiguously bonded. The structure of **12** was confirmed by X-ray crystallography.[9] The dihydrotetrazolo[1,5-*b*][1,2,4]triazine, **10a**, was converted to the 8-nitro derivative, **13**, under similar conditions. It is interesting to compare the stability of compound **12** to that of 5-nitraminotetrazoles such as **13** and **14** and its furazan analogue **15**. Compound **12** is considerably less stable than compounds **13** and **14**. Compound **14** decomposes rapidly at 160 °C, **13** decomposes rapidly at 126 °C and **12** at 104 °C. Thus it would appear that a 1-nitraminotetrazole is kinetically less stable than a 5-nitraminotetrazole. Compound **15** melts then decomposes above 138 °C. The difference in the heat of formation of **12** and **11a** has been determined to be 54 kcal/mol, while the difference between **15** and its precursor **16** has been determined to be 44 kcal/mol.[10] Thus it would appear that nitramino groups attached to tetrazole rings at the 1-position are kinetically and thermodynamically less stable than those attached to furazan rings.



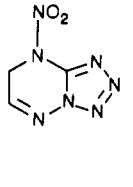


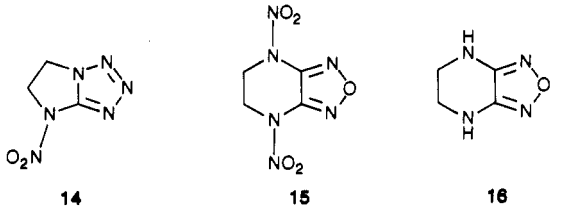
Table I. Synthesis of Tetrazolo[1,5-*b*][1,2,4]triazines

compound	yield, %
6a: R_1, R_2 = H	70–73
6b:[a] R_1 = CH_3; R_2 = H	85
6c:[a] R_1 = H; R_2 = CH_3	
6d: R_1, R_2 = CH_3	90

[a] 50:50 mixture of **6b** and **6c**.

Table II. Synthesis and Properties of 7,8-Dihydrotetrazolo[1,5-*b*][1,2,4]triazines

compound	mp, °C	yield, %
10a: R_1 = R_2 = H	161	70
10c: R_1 = H; R_2 = CH_3	137	66
10d: R_1 = R_2 = CH_3	133	50



Experimental Section

^1H NMR spectra were recorded on a Varian EM-360A NMR spectrometer and are referenced to TMS. IR spectra were recorded on a Nicolet 6000 FTIR spectrometer either as films (liquids) or KBr pellets (solids). Melting points (decomposition points) were measured on a Du Pont 910 DSC coupled to a Du Pont 1090 thermal analyzer at 10 °C/min. Elemental analyses were carried out by Micro Analysis, Inc., Wilmington, DE. All new compounds gave satisfactory C, H, and N analyses (±0.4%).

Tetrazolo[1,5-*b*][1,2,4]triazines (6a–d). In a 250-mL round-bottom flask, equipped with a reflux condenser and magnetic stir bar, was placed 18.12 g (0.125 m) of 40% aqueous glyoxal, 1 mL of concentrated hydrochloric acid, and 125 mL of water. This solution was stirred, and the temperature was raised to 60 °C. DAT, (10 g, 0.1 mol) was added in small portions over 5 min. The solution was then refluxed for 30 min and cooled, and crude product was collected and dried. The crude product was recrystallized from methanol to give the pure product. In a similar fashion, a mixture of **6b** and **6c** was synthesized from pyruvic aldehyde and **6d** from biacetyl. The yields are summarized in Table I.

DAT-Glyoxal Diimine (8). The same procedure discussed for the synthesis of a **6a–d** was used except the amount of DAT was doubled and the products were collected while the reaction was still hot, ~60 °C. Compound **8** does not melt but decomposes above 200 °C. Reaction of **6a** and DAT (1:1 molar ratio) under the same conditions also gives **8**. ^1H NMR (DMSO-d_6 60 °C): δ 7.2 (s, 4 H), 7.9 (d, J = 9.0 Hz, 1 H), 8.6 (d, J = 9.0 Hz, 1 H).

7,8-Dihydrotetrazolo[1,5-*b*][1,2,4]triazines (10a,c,d). In a 500-mL Parr hydrogenation bottle was placed 2.0 g of tetrazolo[1,5-*b*][1,2,4]triazine, **6a**, 250 mL of methanol, and 1 g of 5% Pd/C. The mixture was stirred for 15 min to dissolve the starting material and then it was hydrogenated at 60 psi for 1 h. A stream of nitrogen was run through the solution for a few minutes. Then it was heated to reflux and filtered through a fiberglass filter to remove the catalyst. The solvent was removed at reduced pressure to give the crude product, which was recrystallized from methanol to give the pure product. In a similar fashion **6c** and **6d** were

(8) Rheingold, A. L. University of Delaware, private communication. Monoclinic, $P2_1/c$, a = 9.847 (2) Å, b = 6.326 (1) Å, c = 10.791 (2) Å, β = 100.42 (2)°, Z = 4, R = 3.55%.

(9) Rheingold, A. L. University of Delaware, private communication. Monoclinic, $P2_1/c$, a = 9.160 (3) Å, b = 6.911 (3) Å, c = 12.728 Å, β = 90.15 (2)°, Z = 4, R = 4.10%.

(10) Willer, R. L. Synthesis of High-Nitrogen-Content Heterocyclic Nitramines and Energetic Internal Plasticizers. Prepared for Air Force Office of Scientific Research, AFOSR TR-87-0869, AD A182898, 1987.

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Table III. Synthesis and Properties of 5,6,7,8-Tetrahydrotetrazolo[1,5-*b*][1,2,4]triazines

compound	mp, °C	yield, %
11a: $R_1 = R_2 = H$	147	95
11b: $R_1 = CH_3$; $R_2 = H$	141	
11c: $R_1 = H$; $R_2 = CH_3$	125	92
11d: $R_1 = R_2 = CH_3$ (cis)	131	
11e: $R_1 = R_2 = CH_3$ (trans)	164 dec	98

reduced to **10c** and **10d**. The yields and melting points are summarized in Table II. ^{1}H NMR: **10a** (DMSO-d_6) δ 4.20 (d, J = 2.0 Hz, 2 H), 7.4 (t, 1 H, J = 2.0 Hz), 7.85 (br s, 1 H). **10c** ($(CD_3)_2CO$) δ 1.50 (d, J = 6.0 Hz, 3 H), 3.0 (br s, 1 H), 4.68 (dxq, J = 2.0, J = 6.0 Hz, 1 H), 7.4 (d, J = 2.0 Hz, 1 H). **10d** ($(CD_3)_2CO$) δ 1.50 (d, J = 6.0 Hz, 3 H), 2.20 (s, 3 H), 4.50 (q, J = 6.0 Hz, 1 H), 7.3 (br s, 1 H).

5,6,7,8-Tetrahydrotetrazolo[1,5-*b*][1,2,4]triazines (11a-e). In a 250-mL Erlenmeyer flask equipped with a thermometer and stirring bar was placed 1.22 g (10 mmol) of tetrazolo[1,5-*b*]-[1,2,4]triazine, **6a**, and 50 mL of methanol. This solution (slurry) was stirred, and the temperature was adjusted to 10 °C (ice bath); then sodium borohydride 0.5 g (13 mmol) was added in one portion. After the mixture was stirred for 30 min, the methanol was removed at reduced pressure, 50 mL of water was added, and this was removed at reduced pressure. The resulting solid was recrystallized from a mixture of water to give the pure product. In a similar fashion a mixture of **6b** and **6c**, pure **6c** and **6d** were reduced to give respectively a mixture of **11b** and **11c**, pure **11c**, and a mixture of **11d** and **11e**. The yields and melting points of the products are summarized in Table III. ^{1}H NMR: **11a** (DMSO-d_6) δ 3.30 (m, 4 H), 7.00 (t, J = 6.0 Hz), 7.70 (br s, 1 H). **11b** ($(CD_3)_2CO$) δ 1.25 (d, J = 6.0 Hz, 3 H), 2.90-3.80 (m, 3 H), 6.2 (d, J = 10.0 Hz, 1 H, exchanges), 6.80 (br s, 1 H). **11c** ($(CD_3)_2CO$) δ 1.30 (d, J = 6.0 Hz, 3 H), 2.90-3.80 (m, 3 H), 6.70 (dxd, J = 3.0 Hz, J = 9.0 Hz, 1 H), 7.30 (br s, 1 H). **11d** ($(CD_3)_2CO$) δ 0.95 (d, J = 6.0 Hz, 3 H), 1.05 (d, J = 6.0 Hz, 3 H), 2.9-3.7 (m, 2 H), 7.15 (d, J = 5.0 Hz, 1 H), 7.75 (br s, 1 H). **11e** ($(CD_3)_2CO$) δ 1.05 (d, J = 6.0 Hz, 3 H), 1.15 (d, J = 6.0 Hz, 3 H), 2.3-3.2 (m, 2 H), 6.75 (d, J = 10.0 Hz, 1 H), 7.25 (br s, 1 H).

5,8-Dinitro-5,6,7,8-tetrahydrotetrazolo[1,5-*b*][1,2,4]triazine (12). In a 25-mL round-bottom flask equipped with a magnetic stirring bar was placed 8.0 mL of 100% nitric acid. This was cooled to 0 °C, and 4 mL of acetic anhydride was added dropwise over 2 min. This mixture was stirred for 10 min. The temperature was then lowered to -20 °C, and 1.26 g (10.0 mmol) of **11a** was added in small portions over 10 min. The mixture was stirred at 0 °C for 10 min and then quenched on ice. After the ice melted, the crude product was isolated by filtration and dried in a vacuum to give 2.1 g (9.5 mmol, 95%) of crude product. The product can be recrystallized by dissolving it in acetone at room temperature and precipitating it out by adding water. The purified product has a mp of 102-104 °C dec. ^{1}H NMR ($(CD_3)_2CO$) δ 4.60 (t, 2 H, J = 5.5 Hz), 5.00 (t, 2 H, J = 5.5 Hz).

8-Nitro-7,8-dihydrotetrazolo[1,5-*b*][1,2,4]triazine (13). Nitration of 0.62 g (5 mmol) of **10a** with acetic anhydride (4 g) and nitric acid (8.0 g) by the procedure described for **12** gave 0.82 g (4.7 mmol, 95%) of **13**. The compound decomposes when recrystallized. The melting point of the crude product is 124-126 °C dec. ^{1}H NMR ($(CD_3)_2CO$) δ 5.50 (d, J = 2.0 Hz, 2 H), 8.2 (t, J = 2.0 Hz, 1 H).

7-Nitro-5,6-dihydro-7*H*-imidazolo[1,2-*d*]tetrazole (14). In a 25-mL ratio round-bottom flask equipped with a magnetic stirring bar was placed 10 g of acetic anhydride. This was cooled to 0 °C (salt-ice bath), and 10 g 100% nitric acid was added dropwise over 10 min. This nitrating solution was stirred for 20 min; then 5.55 g (50 mmol) of 5,6-dihydro-7*H*-imidazolo[1,2-*d*]-tetrazole[11] was added in small portions over 10 min. The solution was stirred for 20 min and then quenched on 50 g of crushed ice. The crude product was collected, washed with water, and dried. The yield was 5.9 g of colorless crystals (37 mmol; 75% yield). Recrystallization from acetone-water gave the pure product, mp 160 °C dec. ^{1}H NMR (CD_3SOCD_3) δ 4.75 (m, 2 H, H_5), 5.05 (m, 2 H, H_6).

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Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters for **11b** and **12** and diagrams with atom numbering (2 pages). Ordering information is given on any current masthead page.

An Unusual Ring Reorganization of a *N*-Styrylisothiazolethione to a 2-Styrylthiazole

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Although the excited-state rearrangement of isothiazoles to thiazoles and the reverse reaction have been well documented,[2] the ground-state version of this type of rearrangement has never been reported so far. We now report the first example of this skeletal reorganization reaction.

In the course of our synthetic efforts on 1,4-thiazepine systems,[3] we have found that attempted Pummerer reaction of 2,3-dihydro-2,7-diphenyl-5-methoxy-1,4-thiazepine 1-oxide (**1**) gave 3-oxo-5-phenyl-(*Z*)-*N*-styrylisothiazole, which, on heating, was quantitatively isomerized to the corresponding *E* isomer (**2**).[4] Treatment of **2** with phosphorus pentasulfide gave a fairly labile product in 78% yield, which could not be purified fully. Nevertheless, the structure of this product can safely be assigned to the expected 3-thioxo-5-phenyl-(*E*)-*N*-styrylisothiazole (**3**) as inferred from the available spectral data. Thus, the ^{1}H NMR spectrum of **3** definitely shows the presence of a β-substituted (*E*)-styryl grouping as exemplified by an AB quartet at δ 6.08 and 7.92 with J_{AB} = 14.3 Hz. Furthermore, the IR spectrum of **3** reveals a thiocarbonyl absorption at 1178 cm^{-1} instead of the corresponding carbonyl absorption at around 1660 cm^{-1}.[4] These spectral findings strongly suggest that no skeletal rearrangement occurred during the reaction of **2** with phosphorus pentasulfide (Scheme I).

To convert the thione **3** into the isothiazolium ion salt **4**, compound **3** was treated with trimethyloxonium tetrafluoroborate in dichloromethane at room temperature for 2 h. Instead of the anticipated product (i.e., 3-(methyl-

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