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SYNTHESIS AND REACTIVITY OF *N*-VINYL-1,2,3-DITHIAZOLIMINES

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Abstract – A reaction of 4,5-dichloro-1,2,3-dithiazolium chloride (Appel salt) (**1**) with aziridines (**2a-d**) affords the *N*-vinyl-1,2,3-dithiazolimines (**3a-d)**, which can be transformed into thiazole derivatives.

INTRODUCTION

1,2,3-Dithiazolimines are of considerable interest in the synthesis of biologically active compounds.[1] In addition, the reactive 1,2,3-dithiazole ring in dithiazolimines can be transformed into various compounds, including heterocyclic structures.[2]

1,2,3-Dithiazolimines are prepared by the reactions of readily accessible 4,5-dichloro-1,2,3-dithiazolium chloride (**1**) (Appel salt) with amines.[1,2] The reactions are accompanied by elimination of two hydrogens from one nitrogen atom of the substrate to form dithiazolimines. Poorly known processes involving elimination of two protons from different atoms of the substrate would be a substantial extension of this approach. Earlier, we have demonstrated that such reactions occur between *N*-monosubstituted aldehyde hydrazones and Appel salt.[3]

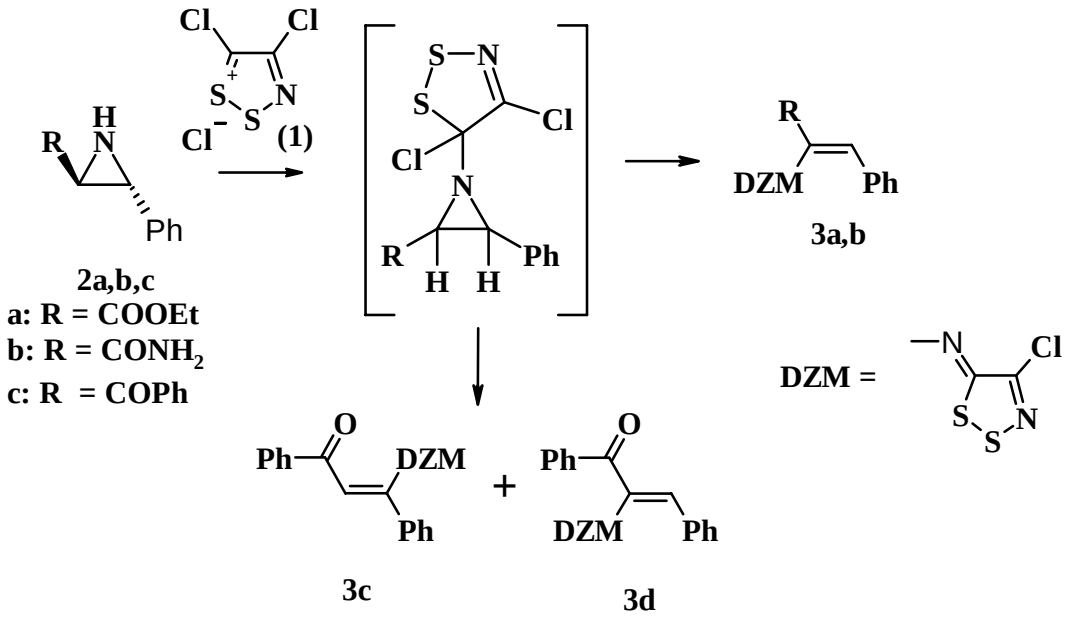
RESULTS AND DISCUSSION

In the present study, we developed a procedure for the synthesis of new *N*-vinyl-1,2,3-dithiazolimines from aziridines, which involves elimination of hydrogens from different nitrogen and carbon atoms. The

reaction of Appel salt (**1**) with aziridinecarboxylic acid ester or amide (**2a**,**b**) having the *trans*-configuration[4] produces one of the possible isomers (Scheme 1). Apparently, the aziridine ring opening occurs almost in parallel with the formation of the double bond.

The NOESY spectrum of dithiazolimine (**3a**) shows the H/CH_3 (7.08/1.22), H/CH_2 (7.08/4.21), and H_{ortho}/CH (7.61/7.22) correlation peaks, which confirm the *cis*- orientation of this vinyl proton with respect to the ester group and the geminal arrangement of the proton and the benzene ring. The *cis*-arrangement is also evidenced by the fact that the GATED ^{13}C NMR spectrum shows a doublet of triplets at δ 124.15 with the constants J(C/CH_2)/JC/CH(Ar) = 158.64/5.13 Hz. The GATED ^{13}C NMR spectrum of dithiazolimine (**3b**) has a doublet of triplets at δ 141.63 with the constants J(C/NH_2)/J(C/CH(Ar)) = 156.89/4.88 Hz, which is indicative of the geminal arrangement of the proton and the benzene ring at the carbon atom and the *cisoid* arrangement of the amide group and this proton, as in the above structure (**3a**). By contrast, the reaction of Appel salt (**1**) with aziridine (**2c)**, which also has the *trans*- configuration,[5] affords two isomeric 1,2,3-dithiazolimines (**3c**) and (**3d**) with ratio 1:9 according NMR spectra (Scheme 1). The signals in the NMR spectra of the resulting compounds are not contradictory to structures (**3c**) or (**3d**). However, they do not allow us to decide between these structures. The position of the dithiazolimine fragment was determined based on further transformations of compound (**3d**) into thiazolyltetrazole (**7d**) and thiazole (**6d**) and the transformation of product (**3c**) into thiazole (**6c**) (Scheme 2).

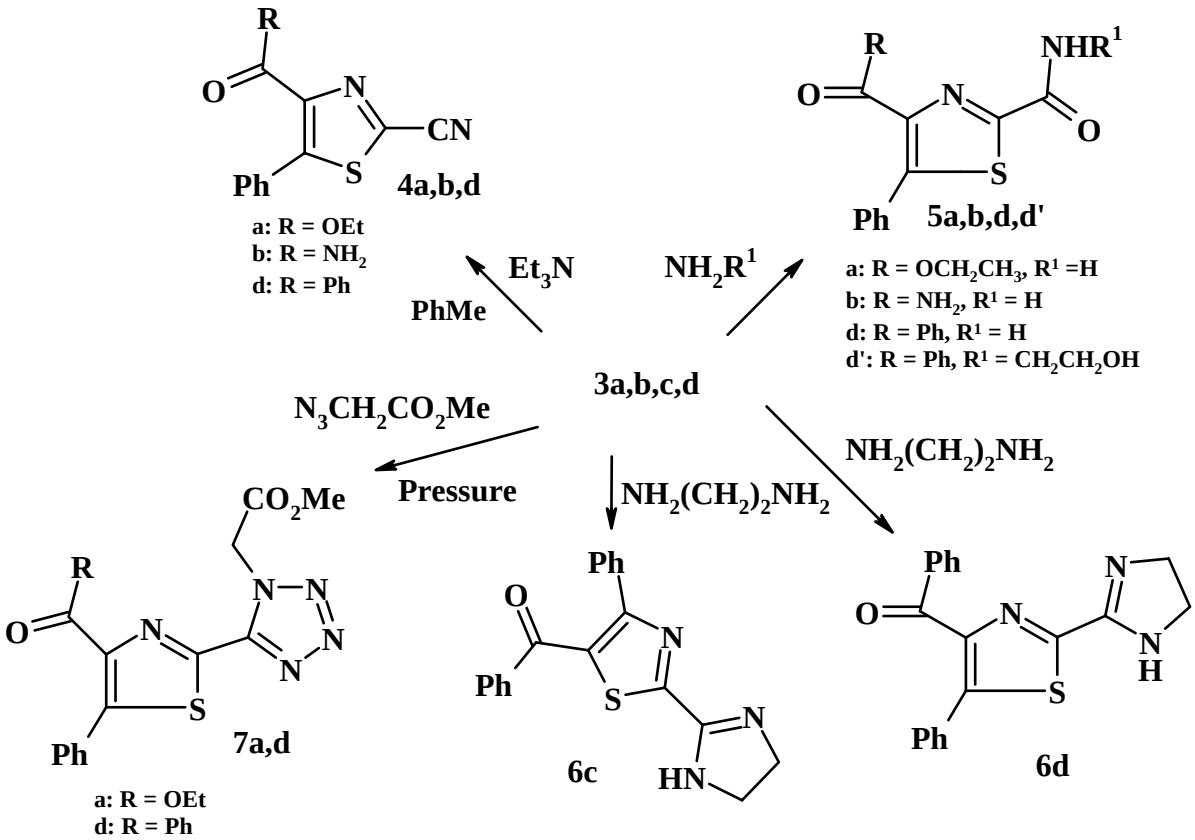
Scheme 1



We studied the reactivity of the resulting dithiazolimines. Earlier, transformations of compounds, in which the dithiazole fragment is conjugated with the *N*-vinyl fragment, in the presence of nucleophiles or on heating have not been investigated. We found that refluxing of dithiazolimines (**3a,b,d**) in toluene in

the presence of triethylamine afford 4-benzoyl-2-cyano-5-phenyl-1,3-thiazoles (**4a,b,d)**. The reactions of dithiazoles (**3a-d)** with ammonia or aminoethanol in tetrahydrofuran produce thiazoles (**5a,b,d,d'**) containing amido groups, whereas the reactions with ethylenediamine give dihydroimidazolylthiazoles (**6c,d**). Earlier, it has been demonstrated that the reactions of amines with iminodithiazoles containing no adjacent substituents afforded only products of the dithiazole ring cleavage.[2] The reactions of dithiazolimines with azidoacetate at 10 kbar and 110°C or in the presence of dibutyltin oxide Bu_2SnO at 70 - 80 °C and 5 kbar give tetrazoles (**7a,d)**. Apparently, azide reacts with the imine fragment of the dithiazole ring activated by the chlorine atom rather than with the nitrile group, because our attempts to prepare the tetrazole moiety from compound (**4d)** by the reaction with azidoacetate under the same conditions failed.

Scheme 2



The structures of thiazolyltetrazoles (**7a,d)** were established by spectroscopic methods. The structure of compound (**7d)** was confirmed by X-Ray diffraction analysis (Figure 1) The tetrazole and thiazole rings in compound (**7d)** are planar and are twisted with respect to each other by 20°. The ethylacetate group in the tetrazole fragment is in the *ortho* position with respect to the thiazole substituent. Apparently, the electronic systems of the heterocycles participate is the π-conjugation.

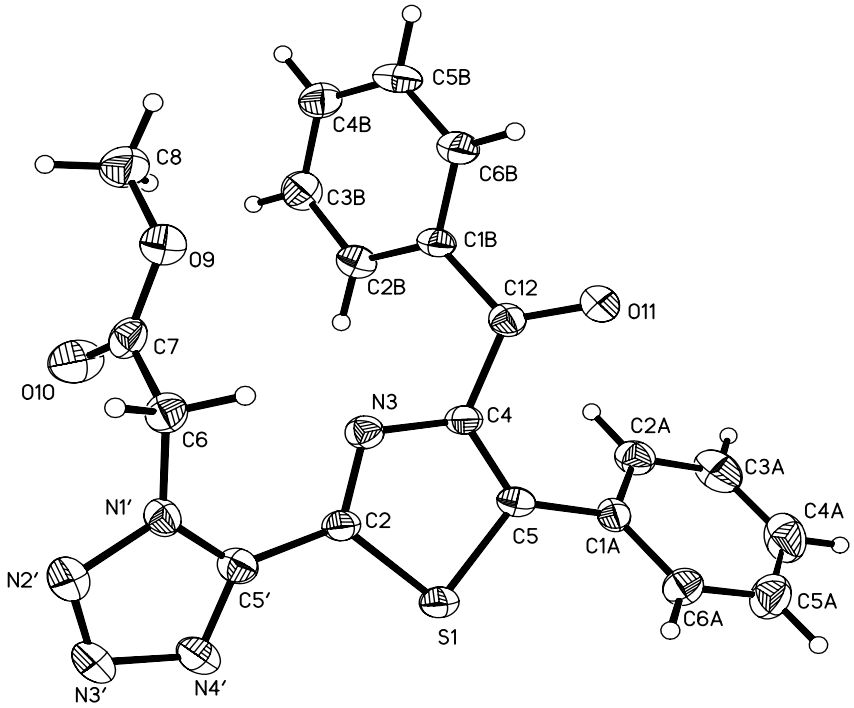


Figure 1. ORTEP drawing of **7d**

To summarize, we developed a procedure for the synthesis of new dithiazolimine and thiazole derivatives. It should be noted that published methods for the synthesis of these thiazoles (for example, the Hantzsch reaction) are difficult to use because the synthesis of most thioamides required for these reactions was not described and is a rather complex problem. It should also be noted that the reactions involving azides can also be considered as a new approach to the synthesis of tetrazole derivatives.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker WM-200 (200 MHz) and Bruker WM-250 (250 MHz) instruments in DMSO-d_6 and $CDCl_3$ relative to HMDS. The MS spectra were obtained on a Varian MATCH-6 instrument with direct sample injection into the ion source; the ionization energy was 70 eV; the accelerating voltage was 1.75 kV. The melting points were measured on a Boetius hot-stage apparatus. The reactions at high pressure were carried out in Teflon tubes on an apparatus described earlier.[6]

Synthesis of dithiazolimines (3a-c). Pyridine (790 mg, 10 mmol) was added dropwise with stirring to a mixture of aziridine (**2a-c**) (5 mmol) and Appel salt (**1**) (1.04 g, 5 mmol) in dichloromethane (30 mL) at rt for 5 min. Then the reaction mixture was stirred for 3 h, the solvent was removed in vacuo, and the residue was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate 1:20).

Ethyl 2-(4-chloro-[1,2,3]-dithiazol-5-ylideneamino)-3-phenylacrylate (3a). Yield 72%; oil; ^{1}H-NMR δ: 1.24 (t, 3 H, *J*=7.21 Hz, CH_3), 4.22 (q, 2 H, *J*=7.21 Hz, CH_2), 7.13 (s, 1 H, CH), 7.38 (m, 3 H, H_{arom}), 7.66 (m, 2 H, H_{arom}); ^{13}C-NMR (50 MHz) δ: 14.09 (CH3), 61.64 (O-CH2), 124.15 (Ph-CH=), 128.69 (o), 129.30 (p), 130.37 (m), 133.50 (i), 138.09 (=C-N=), 145.68 (C-4), 161.58 (C=O), 162.28 (C-5). Anal. Calcd for $C_{13}H_{11}N_2O_2ClS_2$: C, 47.78; H, 3.39; N, 8.57; Cl, 10.85; S, 19.62. Found: C, 47.88; H, 3.42; N, 8.46; Cl, 10.73; S, 19.75. MS, *m/z* 326 (M^+).

2-(4-Chloro-[1,2,3]-dithiazol-5-ylideneamino)-3-phenylacrylamide (3b). Yield 58%; mp 174-176 °C; ^{1}H-NMR δ: 5.93 (s, 1 H, NH), 6.51 (s, 1 H, NH), 7.23 (s, 1 H, H_{arom}), 7.26-7.53 (m, 5 H, H_{arom}); ^{13}C-NMR (50 MHz) δ: 119.18 (=C-N=), 128.61 (o), 130.37 (p), 130.65 (m), 133.31(i), 141.63 (Ph-CH=), 148.97 (C-4), 171.35 (C-5), 172.51 (C=O). Anal. Calcd for $C_{11}H_8N_3OClS_2$: C, 44.37; H, 2.71; N, 14.11; Cl, 11.91; S, 21.53. Found: C, 44.51; H, 2.73; N, 14.16; Cl, 11.87; S, 21.65. MS, *m/z* 297 (M^+).

2-(4-Chloro-[1,2,3]-dithiazol-5-ylideneamino)-1,3-diphenylpropenone (3d). Yield 63%; oil; ^{1}H-NMR δ: 6.81 (s, 1 H, H_{arom}), 7.36-7.89 (m, 10 H, H_{arom}); ^{13}C-NMR (50 MHz) δ: 128.02 (Ph-CH=), 128.55, 128.67, 129.37, 129.52, 130.84, 133.03, 133.81, 136.81, 145.03 (C-N=), 145.94 (C-4), 161.18 (C-5), 190.95 (C=O). Anal. Calcd for $C_{17}H_{11}N_2OClS_2$: C, 56.90; H, 3.09; N, 7.81; Cl, 9.88; S, 17.87. Found: C, 57.12; H, 3.07; N, 7.88; Cl, 9.77; S, 17.95. MS, *m/z* 359 (M^+). The assignment of the 13C chemical shifts was made based on the published data.[7]

General procedure for the synthesis of cyanothiazoles (4a,b,d). A mixture of toluene (5 mL), triethylamine (2.18 g, 23 mmol, 3 mL) and dithiazolimine (**3a,b,d**) (100 mg) was refluxed for 8 h. Then the toluene was removed in vacuo and the residue was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate 1:4).

Ethyl 2-cyano-5-phenylthiazole-4-carboxylate (4a). Yield 83%; mp 108-109 °C; ^{1}H-NMR δ: 1.14 (t, 3 H, *J*=7.09 Hz, CH_3), 4.23 (q, 2 H, *J*=7.11 Hz, CH_2), 7.44-7.60 (m, 5 H, H_{arom}); ^{13}C-NMR (50 MHz) δ: 13.62, 61.35, 112.38, 128.47, 128.98, 129.21, 129.88, 138.08, 141.79, 150.85, 160.143. Anal. Calcd for $C_{13}H_{10}N_2O_2S$: C, 60.45; H, 3.90; N, 10.85; S, 12.41 Found: C, 60.57; H, 3.92; N, 10.71; S, 12.58. MS, *m/z* 258 (M^+).

2-Cyano-5-phenylthiazole-4-carboxamide (4b). Yield 75%; mp 163-165 °C; ^{1}H-NMR δ: 7.48-7.66 (m, 5 H, H_{arom}), 7.99 (s, 2 H, NH_2); ^{13}C-NMR (50 MHz), δ: 112.60, 128.20, 128.46 129.74, 129.91, 132.70, 145.78, 146. 87, 162.21. Anal. Calcd for $C_{11}H_7N_3OS$: C 57.63, H 3.08, N 18.33, S 13.99. Found: C 57.81, H 3.05, N 18.23, S 14.08. MS, *m/z* 229 (M^+).

4-Benzoyl-5-phenylthiazole-2-carbonitrile (4d). Yield 90%; mp 65-67 °C; ^{1}H-NMR δ: 7.41-7.89 (m, 10 H, H_{arom}); ^{13}C-NMR (50 MHz) δ: 112.75, 127.09, 127.85, 128.74, 129.15, 129.47, 130.11, 130.39, 133.74, 134.23, 135.89, 148.75, 188.71. Anal. Calcd for $C_{17}H_{10}N_2OS$: C, 70.33; H, 3.47; N, 9.65; S, 11.04. Found: C, 70.46; H, 3.45; N, 9.56; S, 11.21. MS, *m/z* 290 (M^+).

General procedure for the synthesis of 2-thiazolecarboxamides (5a,b,d,d'). A 25% aqueous ammonia solution (5 mL) was added with stirring to a solution of dithiazolimine (**3a,b,d**) (100 mg) in THF (10 mL). The reaction mixture was stirred at rt for 3 h. Then water and THF were removed *in vacuo* and the residue was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate 1:4).

Ethyl 2-carbamoyl-5-phenylthiazole-4-carboxylate (5a). Yield 77%; mp 153-155°C; ^{1}H-NMR δ: 1.12 (t, 3 H, *J*=7.22 Hz, CH_3), 4.19 (q, 2 H, *J*=7.22 Hz, CH_2), 7.48-7.54 (m, 5 H, H_{arom}), 9.82 (s, 1 H, NH), 10.26 (s, 1 H, NH); ^{13}C-NMR (50 MHz) δ: 13.24, 60.54, 127.96, 129.17, 140.65, 148.81, 159.86, 160.82, 161.90. Anal. Calcd for $C_{13}H_{12}N_2O_3S$: C, 56.51; H, 4.38; N, 10.14; S, 11.60. Found: C, 56.62; H, 4.40; N, 10.07; S, 11.79. MS, *m/z* 276 (M^+).

5-Phenylthiazole-2,4-dicarboxylic acid diamide (5b). Yield 56%; mp 54-56 °C; ^{1}H-NMR δ: 7.49 (m, 5 H, H_{arom}), 9.91 (s, 1 H, NH), 10.32 (s, 1 H, NH); ^{13}C-NMR (50 MHz) δ: 128.48, 129.57, 129.71, 141.43, 152.21, 161.46, 166.53, 185.77. Anal. Calcd for $C_{11}H_9N_3O_2S$: C, 53.43; H, 3.67; N, 16.99; S, 12.97. Found: C, 53.54; H, 3.65; N, 16.84; S, 13.08. MS, *m/z* 247 (M^+).

4-Benzoyl-5-phenylthiazole-2-carboxamide (5d). Yield 78%; mp 119-121 °C; ^{1}H-NMR δ: 7.28-7.88 (m, 10 H, H_{arom}), 7.99 (s, 1 H, NH), 8.26 (s, 1 H, NH); ^{13}C-NMR (50 MHz) δ: 128.79, 128.99, 129.14, 129.41, 129.61, 130.11, 134.02, 136.18, 146.45, 148.15, 160.52, 162.28, 189.90. Anal. Calcd for $C_{17}H_{12}N_2O_2S$: C, 66.22; H, 3.92; N, 9.08; S, 10.40. Found: C, 66.34; H, 3.89; N, 8.93; S, 10.51. MS, *m/z* 308 (M^+).

Synthesis of 4-benzoyl-N-(2-hydroxyethyl)-5-phenyl-1,3-thiazole-2-carboxamide (5d'). Ethanolamine (860 mg, 14mmol, 1 mL) was added with stirring to a solution of dithiazolimine (**3d**) (100 mg, 0.28 mmol) in THF (10 mL). The reaction mixture was stirred at rt for 8 h, after which THF was removed *in vacuo* and the residue was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate 1:4). Yield 79%; oil; ^{1}H-NMR δ: 3.58 (br s, 4 H, $2CH_2$), 7.27-7.88 (m, 10 H, H_{arom}); ^{13}C-NMR (50 MHz) δ: 42.06, 59.33, 128.15, 128.51, 128.94, 129.51, 130.00, 133.14, 136.13, 148.04, 156.71, 158.69, 161.94, 164.91, 189.99. Anal. Calcd for $C_{19}H_{16}N_2O_3S$: C, 64.76; H, 4.58; N, 7.95; S, 9.10. Found: C, 64.89; H, 4.56; N, 7.88; S, 9.22. MS, *m/z* 352 (M^+).

[2-(4,5-Dihydro-1*H*-imidazol-2-yl)-5-phenylthiazol-4-yl]phenylmethanone (6d). A mixture of dithiazolimine (**3d**) (200 mg, 0.55 mmol) and ethylenediamine (500 mg, 0.56 mL, 8.3 mmol) in THF (10 mL) was stirred at rt for 20 h, after which THF was removed *in vacuo* and the residue was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate 1:4). Yield 73%; mp 167-169 °C; ^{1}H-NMR δ: 3.98 (s, 4 H, $2CH_2$), 7.41-7.92 (m, 10 H, H_{arom}); ^{13}C-NMR (50 MHz) δ: 45.92 (-CH2-CH2-), 128.14, 128.49, 129.00 (p), 129.27, 129.49, 132.67 (=N-C=), 133.64 (p), 133.37 (i), 136.64 (i), 156.86 (=C-Ph), 158.55 (-N=C-NH-), 160.63 (-N=C-S-), 188.91 (C=O). Anal. Calcd for $C_{19}H_{15}N_3OS$: C, 68.45; H, 4.53; N, 12.60; S, 9.62. Found: C, 68.58; H, 4.51; N, 12.45; S, 9.74. MS, *m/z* 333 (M^+).

[2-(4,5-Dihydro-1*H*-imidazol-2-yl)-4-phenylthiazol-5-yl]phenylmethanone (6c). A mixture of two dithiazolimines (**3d**) and (**3c**) (1 g, 2.8 mmol), which were prepared according to the above-described procedure, was dissolved in tetrahydrofuran (30 mL) and then ethylenediamine (2 g, 2.24 mL, 33.2 mmol) was added. The reaction mixture was stirred at rt for 20 h and worked up analogously to compound (**6d**). Compounds (**6d**) and (**6c**) were prepared in yields of 610 mg (66%), and 66 mg, (7%), respectively; mp 108-110 °C; ^{1}H-NMR δ: 3.69 (s, 4 H, 2CH_2), 7.24-7.69 (m, 10 H, H_{arom}); ^{13}C-NMR (50 MHz) δ: 45.91(-CH_2-CH_2-), 128.42 (-S-C=), 128.99, 129.39, 130.33, 130.43, 134.50, 136.01, 148.14, 148.43 (-N=C-S-), 148.98, 157.41 (-N=C-NH-), 189.57 (C=O). Anal. Calcd for $C_{19}H_{15}N_3OS$: C, 68.45; H, 4.53; N, 12.60; S, 9.62. Found: C, 68.56; H, 4.50; N, 12.47; S 9.71. MS, *m/z* 333 (M^+).

Synthesis of thiazolyltetrazoles (7a,d). A mixture of dithiazolimine (**3a**) or (**3d**) (100 mg) and methyl azidoacetate (160 mg, 1.4 mmol) in acetonitrile (3 mL) was kept at 110 °C and 10 kbar for 8 h. Tetrazoles were purified by thin layer chromatography (SiO_2, ethyl acetate/hexane 1:1) and crystallized from acetone.

Ethyl 2-(1-methoxycarbonylmethyl-1*H*-tetrazol-5-yl)-5-phenylthiazole-4-carboxylate (7a). Yield 63%; mp 91-93 °C; ^{1}H-NMR δ: 1.19 (t, 3 H, *J*=7.20 Hz, CH_3), 3.89 (s, 3 H, CH_3), 4.21 (q, 2 H, *J*=7.22 Hz, CH_2), 5.87 (s, 2 H, CH_2), 7.51-7.62 (m, 5 H, H_{arom}); ^{13}C-NMR (50 MHz) δ: 13.63, 50.25, 52.80, 61.16, 128.35, 128.46, 129.83, 129.99, 141.72, 147.87, 148.34, 148.46, 160.59, 166.56. Anal. Calcd for $C_{16}H_{15}N_5O_4S$: C, 51.47; H, 4.05; N, 18.76; S, 8.59. Found: C, 51.53; H, 4.07; N, 18.82; S, 8.63. MS, *m/z* 373 (M^+).

Methyl [5-(4-benzoyl-5-phenylthiazol-2-yl)tetrazol-1-yl]acetate (7d). Yield 76%; mp 170-171°C; ^{1}H-NMR δ: 2.51 (s, 3 H, CH_3), 5.75 (s, 2 H, CH), 7.47-7.91 (m, 10 H, H_{arom}); ^{13}C-NMR (50 MHz) δ: 50.08, 52.37 128.38, 128.61, 129.06, 129.38, 129.95, 130.05, 133.96, 136.11, 146.45, 148.09. 148.53, 166.46, 188.95. Anal. Calcd for $C_{20}H_{15}N_5O_3S$: C, 59.25; H, 3.73; N, 17.27; S, 7.91. Found: C, 59.43; H, 3.71; N, 17.15; S, 8.22. MS, *m/z* 405 (M^+).

X-Ray diffraction study of thiazolyltetrazole (7d). Colorless transparent single crystals of compound (**7d**) of composition $C_{20}H_{15}N_5O_3S$ were grown from a solution in acetone. The unit cell parameters and intensities of 5452 independent reflections were measured at 295 K on a "CAD4 Enraf-Nonius" diffractometer (MoKα radiation, λ = 0.711 Å, graphite monochromator, *q* –5/3*q*-scanning technique in the angle range 2.04 ≥ θ ≤ 29.97°). The crystallographic data for compound (**7d**): molecular weight M = 405.43, monoclinic system, space group $P2_1/n$, *a* 9.000 (4), *b* 12.366 (5), *c* 16.901 (6) Å, *β* 92.28 (3)˚, *V* 1879.5 (13) Å3 , Z = 4, ρ_{calcd} = 1.433 g/cm^3. The structure was solved by direct methods, which revealed all nonhydrogen atoms. The hydrogen atoms were located from difference electron density maps. The structure was solved by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms. The hydrogen atoms were refined isotropically by the least-squares method. The

final R factors for 1714 reflections with ***I > 2σ(I)*** were R_1 0.068 , wR_2 0.115. The R factors based on all independent reflections were R_1 0.301, wR_2 0.163. The calculations were carried out using the Bruker SMART[8], SHELXL-97, and Bruker SHELXTL[9] program packages. The atomic coordinates, displacement parameters, and geometric characteristics of molecule (**7d**) were deposited at the Cambridge Crystallographic Data Center as supplementary publication numbers 266185.

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