Synthesis and properties of 4-substituted 5*H*-1,2,3-dithiazol-5-ylidenes*

*V. V. Popov, O. I. Bol´shakov, L. S. Konstantinova, and O. A. Rakitin**

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 5328. E-mail: orakitin@ioc.ac.ru

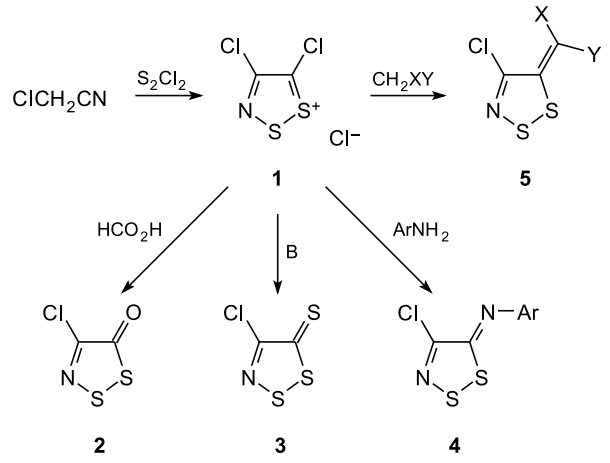
Substituted ethanone oximes react with S_2Cl_2 and pyridine to give 1,2,3-dithiazolium chlorides. The treatment of these products with malonodinitrile in dichloromethane affords 4-substituted 5*H*-1,2,3-dithiazol-5-ylidenes. The reaction of the latter compounds with *n*-butylamine unexpectedly yielded addition products at one of the nitrile groups, *viz.* substituted 1,2,3-dithiazol-5-ylideneethanimidamides.

Key words: 1,2,3-dithiazoles, synthesis, ethanone oximes, sulfur monochloride, malonodinitrile, ethanimidamides.

Derivatives of monocyclic non-fused 1,2,3-dithiazoles are of great interest as herbicides, compounds exhibiting cytotoxic or cytostatic activity, and precursors of molecular semiconductors.[1] 1,2,3-Dithiazoles containing the chlorine atom at position 4 are known and well studied. Various derivatives, including ketone **2**, thione **3**, imines **4**, and ylidenes **5**, were synthesized based on 4,5-dichloro-5*H*-1,2,3-dithiazolium chloride **1** (Scheme 1), and these compounds were used for the synthesis of a wide range of functional derivatives.[1,2]

It should be noted that other 4-substituted 1,2,3-dithiazoles were hitherto virtually unknown. However, these compounds would be expected to have radically different chemical and biological properties due to the absence of the good leaving chlorine atom. Recently, we have developed a general procedure for the synthesis of 4-substituted 1,2,3-dithiazoles by the reaction of readily available ethanone oximes with sulfur monochloride and synthesized a wide range of various ketones, thiones, and imino derivatives of these heterocycles.[3] In the present study, we examined the possibility of synthesizing 4-substituted 5-ylidene-1,2,3-dithiazoles and investigated selected chemical properties of the reaction products.

Scheme 1



B is a base.

Previously, it has been shown[3] that ethanone oximes **6** react with S_2Cl_2 to give 4-substituted 1,2,3-dithiazolium chlorides. It was found that the highest yields of the products were achieved with the use of ethanone oxime **6**, sulfur monochloride, and pyridine in a ratio of 1 : 2 : 3. At the same time it was found that salts **6** are insufficiently stable and decompose with time. Hence, we decided to perform the *in situ* reactions of these compounds with C-nucleophiles.

As a model transformation, we chose the reaction of acetophenone oxime **6a** with S_2Cl_2 followed by the treatment with malonodinitrile as the C-nucleophile containing the active methylene fragment (Scheme 2).

It appeared that the reaction afforded the target product **8a** along with 4-phenyl-1,2,3-dithiazole-5-thione (**9a**) as the by-product. With the aim of finding the optimal conditions for the reaction of salt **7a** with malonodinitrile, we varied the reagent ratio, the temperature, and the reaction time. All three factors were found to influence the yield of the target product **8a**. The main results are presented in Table 1.

The introduction of three equivalents of malonodinitrile and the performance of the reaction at low temperature made it possible to suppress, to a certain

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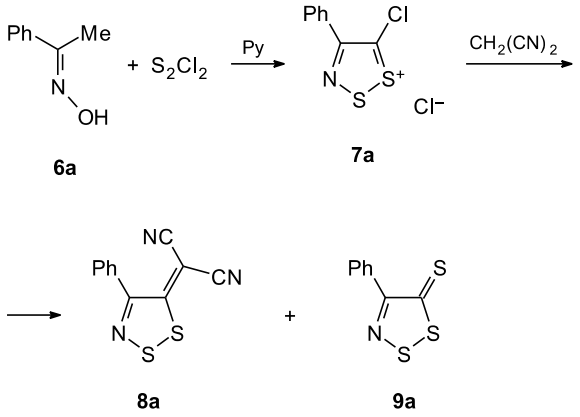
Scheme 2



6a **7a** **8a** **9a**

Table 1. Reaction conditions and the yields of the reaction products of 1-phenylethanone oxime (10 mmol) with S_2Cl_2 (20 mmol), pyridine (30 mmol), and malonodinitrile

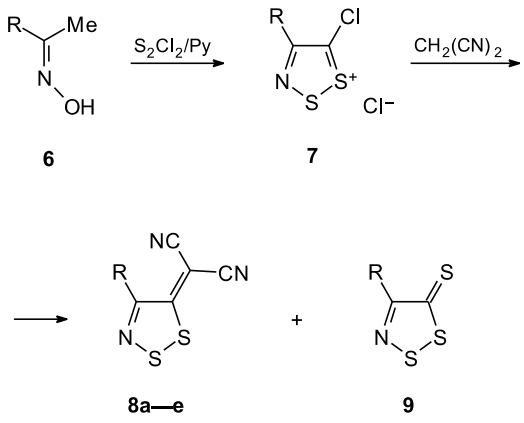
Run	Conditions			Yield (%)	
	$CH_2(CN)_2$ /mmol	*T*/°C	*t*/min	**8a**	**9a**
1	10	–5	30	7	40
2	10	–5	60	7	37
3	10	–5	90	8	33
4	10	–20	60	5	28
5	30	–5	30	8	33
6	30	–20	60	8	23
7	30	–20	90	11	25
8	50	–15	60	17	27
9	50	–15	90	17	27
10	100	–15	90	16	27

extent, the competitive reaction giving rise to thione; however, at –20 °C malonodinitrile also exhibits low activity, as evidenced by the low yields of the target ylidene. Nevertheless, we succeeded in partially suppressing the competitive reaction giving rise to thione **9a** and increased the yield of ylidene **8a** from 7% to 17% by increasing the amount of malonodinitrile in the reaction mixture to the fivefold excess and keeping the reaction mixture at –15 °C for 1 h. However, an increase in the amount of malonodinitrile to the tenfold excess and the storage of the reaction mixture during a longer time (1.5 h) did not allow us to obtain the target product in higher yield. As can be seen from Table 1, the total yield of products **8a** and **9a** remains virtually constant regardless of the reaction conditions, which apparently indicates that the reactions yielding both products are competitive.

Thione **9a** is produced in the reaction of salt **7a** with the sulfur-containing nucleophile. The latter is formed from the base (pyridine), which is present in the reaction mixture, and S_8, which is generated in the course of the reaction (the mechanism was described in the publication[4]). Under these conditions, the activity of this sulfur-containing nucleophile is evidently comparable to the nucleophilicity of malonodinitrile.

We extended the above-described conditions to a series of ethanone oximes and showed that, in most cases, these reactions afford 1,2,3-dithiazol-5-ylidenes although, as a rule, in low yields (Scheme 3). These transformations give the corresponding thiones **9** as by-products.

Scheme 3



6 **7** **8a—e** **9**

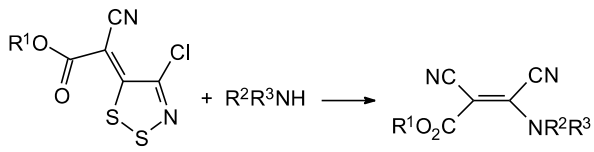
Compound **8**	R	Yield (%)	Compound **8**	R	Yield (%)
a	Ph	17	**d**	2-thienyl	12
b	4-FC_6H_4	14	**e**	Me	23
c	4-$MeOC_6H_4$	14			

It should be noted that Appel's salt **1** containing the electron-withdrawing chlorine atom at position 4 does not react with malonodinitrile even at 0 °C. An increase in the reaction temperature to room temperature results in the slow formation of thione **3**.

It is known[1,2] that the most characteristic reactions of 4-chloro-1,2,3-dithiazol-5-ylidenes are reactions with nucleophilic reagents and reagents with high basicity, which, as a rule, are accompanied by the ring opening and elimination of the chlorine atom as the chloride anion giving rise to the nitrile group. Thus, the reactions of (4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)cyanoacetates **10** with primary and secondary amines produce (*Z*)-3-alkylamino-2,3-dicyanoacrylates **11** in yields from moderate to high.[5] The formation of these compounds can be attributed to the nucleophilic attack of the alkylamine on the carbon atom C(5) of the dithiazole ring accompanied by the elimination of S_2 and HCl and the formation of the stable nitrile group (Scheme 4).

The behavior of trifluoroacetylidene derivatives of 1,2,3-dithiazoles in the reactions with alkylamines somewhat differs from the above-considered reaction. Thus, these derivatives form dihydroaminopyrroles (22—55%)

Scheme 4



10 **11**, 39—72%

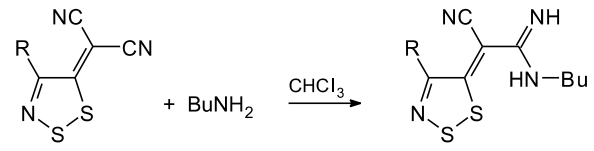
R^1 = Me, Et
R^2, R^3 = H, Me, Et, Pr, Bu, Pr^i, Bu^t, allyl, *n*-pentyl

with primary amines and dihydroiminofurans (18—62%) with secondary amines.[5] However, it is hypothesized that cyanoenamino ketones analogous to (*Z*)-3-alkylamino-2,3-dicyanoacrylates **11** are the key intermediates in these reactions.

We studied the reactions of ylidenes **8** with diethylamine and butylamine. The reactions of ylidenes **8** with diethylamine in chloroform at room temperature were found to afford a series of unstable products, which we failed to isolate and identify.

The reactions of all ylidenes under investigation (**8a—e**) with primary butylamine instead of diethylamine afford one product in moderate yields. We found that two equivalents of amine are necessary for the reaction to proceed. The mass spectra of the reaction products have molecular ion peaks with the mass equal to the sum of the molecular masses of the starting compounds. This fact indicates that these compounds are addition products of the primary amine molecule to dithiazole **8**. The NMR spectra show signals of the dithiazole ring, the corresponding substituents R, and the nitrile group (δ 115—116), whose presence is confirmed also by the presence of the characteristic band (ν 2200—2210 cm^{-1}) in the IR spectrum. Therefore, the reaction proceeds as the addition of the amine molecule to the nitrile group to form the corresponding monoamidines **12** (Scheme 5) rather than according to the mechanism known for 1,2,3-dithiazoles, which involves the ring opening.

Scheme 5



8 **12a—e**

Compound **12**	R	Yield (%)	Compound **12**	R	Yield (%)
a	Ph	42	**d**	2-thienyl	39
b	4-FC$_6$H$_4$	35	**e**	Me	57
c	4-MeOC$_6$H$_4$	42			

This reaction pathway is unusual because only one example of the analogous addition of amine to the dicyanomethylene group is known,[6] whereas amidines **12** are generally synthesized in a more complex way.

Experimental

The ^{1}H NMR spectra (in $CDCl_3$) were recorded on a Bruker AM-300 instrument operating at 300 MHz; the ^{13}C NMR spectra were measured on a Bruker AM-300 instrument operating at 75.5 MHz. The chemical shifts are given on the δ scale with respect to $SiMe_4$. The melting points were determined on a Kofler hot-stage apparatus and are uncorrected. The electron-impact mass spectra were obtained on a Finnigan MAT INCOS 50 instrument (70 eV). The IR spectra were recorded on a Specord M80 instrument in KBr pellets.

The starting ethanone oximes **6a—e** were synthesized according to the general procedure.[7] The melting points and the spectroscopic characteristics of substituted 5*H*-1,2,3-dithiazole-5-thiones **9a**,**b**,**d**,**e** are similar to those described previously.[3]

Synthesis of 4-substituted 5*H*-1,2,3-dithiazol-5-ylidenemalononitriles (general procedure). Sulfur monochloride (0.32 mL, 4 mmol) and pyridine (0.48 mL, 6 mmol) were successively added dropwise to a solution of ethanone oxime **6** (2 mmol) in dichloromethane (15 mL) at −7 °C under argon. The reaction mixture was kept at −2 °C for 20 min, a solution of malonodinitrile (0.66 g, 10 mmol) in acetonitrile (10 mL) was added dropwise at −15 °C, and the reaction mixture was stirred for 1 h. Then pyridine (0.32 mL, 4 mmol) was added dropwise at −15 °C, the temperature was raised to room temperature, and the reaction mixture was concentrated. The residue was chromatographed on a silica gel column (Silicagel Merck 60, CH_2Cl_2—petroleum ether mixture as the eluent).

2-(4-Phenyl-5*H*-1,2,3-dithiazol-5-ylidene)malononitrile (8a). The yield was 17%, R_f = 0.68 (CH_2Cl_2). Orange crystals, m.p. 215—217 °C. Found (%): C, 54.68; H, 2.31; N, 16.91; S, 26.29. $C_{11}H_5N_3S_2$. Calculated (%): C, 54.30; H, 2.07; N, 17.27; S, 26.36. IR, ν/cm^{-1}: 2924, 2852 (C—H), 2216 (CN), 1468, 1280, 1096, 812, 748. ^{1}H NMR ($CDCl_3$), δ: 7.59 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 60.8 ($C(CN)_2$); 111.7 (CN); 117.7 (CN); 128.5 (2 CH_{Ph}); 129.4 (2 CH_{Ph}); 130.8 (CH_{Ph}); 131.0; 161.9; 174.0 (3 C_{quat}). MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 243 [M]$^+$ (57), 179 (35), 135 (90), 103 (100), 77 (100).

4-Phenyl-5*H*-1,2,3-dithiazole-5-thione (9a). The yield was 27%, R_f = 0.93 (CH_2Cl_2).

2-[4-(4-Fluorophenyl)-5*H*-1,2,3-dithiazol-5-ylidene]malononitrile (8b). The yield was 14%, R_f = 0.73 (CH_2Cl_2). Orange crystals, m.p. 224—226 °C. Found (%): C, 50.49; H, 1.50; N, 16.12. $C_{11}H_4FN_3S_2$. Calculated (%): C, 50.65; H, 1.54; N, 15.88. IR, ν/cm^{-1}: 2920 (C—H), 2208 (CN), 1608, 1516, 1448, 1286, 1228, 1164, 1020, 880, 848, 784, 668. ^{1}H NMR ($CDCl_3$), δ: 7.23 (t, 2 H, Ar, *J* = 8.8 Hz); 7.51 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 60.7 ($C(CN)_2$); 111.8 (CN); 115.7 (2 CH); 117.6 (CN); 132.1 (2 CH); 127.5; 161.0; 165.2; 174.4 (4 C_{quat}). MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 273 [M]$^+$ (80), 209 (32), 165 (80), 133 (75), 108 (60).

4-(4-Fluorophenyl)-5*H*-1,2,3-dithiazole-5-thione (9b). The yield was 30%, R_f = 0.92 (CH_2Cl_2).

2-[4-(4-Methoxyphenyl)-5*H*-1,2,3-dithiazol-5-ylidene]malononitrile (8c). The yield was 14%, R_f = 0.60 (CH_2Cl_2).

Orange crystals, m.p. 167—169 °C. Found (%): C, 52.95; H, 2.76; N, 15.35. $C_{12}H_7N_3OS_2$. Calculated (%): C, 52.73; H, 2.58; N, 15.03. IR, ν/cm^{-1}: 3020 and 2928 (C—H), 2196 (CN), 1608, 1516, 1468, 1444, 1416, 1264, 1184, 1028, 808 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ: 3.78 (s, 3 H, MeO); 7.01 (d, 2 H, 2 CH, J = 8.8 Hz); 7.47 (d, 2 H, 2 CH, J = 8.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 55.4 (CH_3); 60.9 ($C(CN)_2$); 111.8 (CN); 117.8 (CN); 113.9 (2 CH, Ar); 131.1 (2 CH, Ar); 123.0; 161.1; 161.9; 174.4 (4 C_{quat}). MS (EI, 70 eV), m/z (I_{rel} (%)): 273 [M]$^+$ (30), 209 (15), 133 (55), 108 (45).

4-(4-Methoxyphenyl)-5*H*-1,2,3-dithiazole-5-thione (8c). The yield was 30%, R_f = 0.89 (CH_2Cl_2). Pale-brown crystals, m.p. 68—71 °C. Found (%): C, 44.95; H, 3.08; N, 6.04. $C_9H_7NOS_3$. Calculated (%): C, 44.79; H, 2.92; N, 5.80. ^{1}H NMR ($CDCl_3$), δ: 3.87 (s, 3 H, CH_3); 6.98 (d, 2 H, 2 CH, J = 8.8 Hz), 8.98 (d, 2 H, 2 CH, J = 8.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 55.4 (CH_3); 113.5 (2 CH, Ar); 123.9 (2 CH, Ar); 131.1; 161.4; 167.3 (3 C_{quat}); 208.4 (C=S). MS (EI, 70 eV), m/z (I_{rel} (%)): 241 M$^+$ (28), 210 (15), 197 (4), 133 (100).

2-(4-Thiophen-2-yl-5*H*-1,2,3-dithiazol-5-ylidene)malononitrile (8d). The yield was 12%, R_f = 0.58 (CH_2Cl_2). Brown crystals, m.p. 160—162 °C. Found (%): C, 43.31; H, 1.16; N, 16.80. $C_9H_3N_3S_3$. Calculated (%): C, 43.66; H, 1.31; N, 16.45. IR, ν/cm^{-1}: 3096, 2924 (C—H), 2204 (CN), 1632, 1444, 1244, 1052, 886, 828, 720, 668 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ: 7.16 (m, 1 H, thienyl); 7.48 (d, 1 H, thienyl, J = 4.8 Hz); 7.84 (d, 1 H, thienyl, J = 5.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 60.0 ($C(CN)_2$); 111.5 (CN); 117.6 (CN); 132.0, 130.7 and 127.3 (3 CH, thienyl); 134.9; 174.1 and 155.4 (3 C_{quat}). MS (EI, 70 eV), m/z (I_{rel} (%)): 249 [M]$^+$ (87), 222 (15), 185 (35), 141 (98), 109 (72), 82 (37).

4-(2-Thienyl)-5*H*-1,2,3-dithiazole-5-thione (9d). The yield was 28%, R_f = 0.90 (CH_2Cl_2).

2-(4-Methyl-5*H*-1,2,3-dithiazol-5-ylidene)malononitrile (8e). The yield was 23%, R_f = 0.70 (CH_2Cl_2). Pale-orange crystals, m.p. 150—152 °C. Found (%): C, 39.71; H, 1.69; N, 23.16. $C_6H_3N_3S_2$. Calculated (%): C, 40.11; H, 1.87; N, 22.88. IR, ν/cm^{-1}: 2920 (CH), 2212 (CN), 1456, 1376, 1272, 1200, 1028, 964, 932, 892, 788, 668 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ: 2.86 (s, 3 H, CH_3). ^{13}C NMR (($CDCl_3$), δ: 20.3 (CH_3); 64.1 ($C(CN)_2$); 112.7 (CN); 116.5 (CN); 160.3 and 173.9 (2 C_{quat}). MS (EI, 70 eV), m/z (I_{rel} (%)): 181 [M]$^+$ (27), 73 (100), 64 (45), 46 (22).

4-Methyl-5*H*-1,2,3-dithiazole-5-thione (9e). The yield was 18%, R_f = 0.95 (CH_2Cl_2).

Synthesis of *N*-butyl-2-cyano-2-(4-R-1,2,3-dithiazol-5*H*-ylidene)acetamidines 12 (general procedure). *n*-Butylamine (0.2 mL, 2 mmol) was added dropwise to a solution of ylidene **8** (1 mmol) in chloroform (30 mL) at room temperature under argon. The reaction mixture was stirred for 2 h and then chromatographed on a silica gel column (Silicagel Merck 60, CH_2Cl_2 as the eluent).

***N*-Butyl-2-cyano-2-(4-phenyl-1,2,3-dithiazol-5-ylidene)-ethanimidamide (12a).** The yield was 42%. Yellow crystals, m.p. 94—96 °C. Found (%): C, 57.23; H, 5.29; N, 17.35. $C_{15}H_{16}N_4S_2$. Calculated (%): C, 56.93; H, 5.10; N, 17.70. IR, ν/cm^{-1}: 3628 and 3212 (NH), 2956, 2928, 2852 (CH), 2206 (CN), 1596, 1448, 1336, 1280, 1196, 872, 740, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ: 0.97 (t, 3 H, CH_3, J = 7.3 Hz); 1.45 (m, 2 H, CH_2); 1.67 (m, 2 H, CH_2); 3.48 (m, 2 H, CH_2); 7.50 (m, 3 H, Ph); 7.74 (m, 2 H, Ph); 8.10 (s, 1 H, NH); 8.42 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 13.7 (CH_3); 20.1 (CH_2); 31.3 (CH_2); 42.3 (CH_2); 116.4 (CN); 126.8 (2 CH, Ph); 128.8 (2 CH, Ph); 130.6 (CH, Ph); 137.3; 155.0, 155.2, 163.3 and 164.5 (5 C_{quat}). MS (EI, 70 eV), m/z (I_{rel} (%)): 316 [M]$^+$ (7), 273 (80), 244 (8), 180 (7), 103 (25), 77 (80).

***N*-Butyl-2-cyano-2-[4-(4-fluorophenyl)-1,2,3-dithiazol-5-ylidene]ethanimidamide (12b).** The yield was 35%. Yellow crystals, m.p. 88—90 °C. Found (%): C, 54.13; H, 4.63; N, 16.46. $C_{15}H_{15}FN_4S_2$. Calculated (%): C, 53.87; H, 4.52; N, 16.75. IR, ν/cm^{-1}: 3316 and 3272 (NH), 3080, 2960, 2928, 2856 (CH), 2207 (CN), 1604, 1556, 1504, 1440, 1236, 1164, 1004, 836, 804, 716, 676. ^{1}H NMR ($CDCl_3$), δ: 0.97 (t, 3 H, CH_3, J = 7.3 Hz); 1.45 (m, 2 H, CH_2); 1.67 (m, 2 H, CH_2); 3.48 (m, 2 H, CH_2); 7.19 (t, 2 H, Ar, J = 8.1 Hz); 7.76 (m, 2 H, Ar); 8.11 (s, 1 H, NH); 8.44 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 13.8 (CH_3); 20.2 (CH_2); 31.5 (CH_2); 42.5 (CH_2); 116.1 (2 CH, Ar); 116.6 (CN); 129.1 (2 CH, Ar); 133.7, 154.2, 162.5, 163.5, 164.5, 165.8 (6 C_{quat}). MS (EI, 70 eV), m/z (I_{rel} (%)): 334 [M]$^+$ (15), 291 (100), 262 (5), 121 (25), 95 (25).

***N*-Butyl-2-cyano-2-[4-(4-methoxyphenyl)-1,2,3-dithiazol-5-ylidene]ethanimidamide (12c).** The yield was 42%. Yellow crystals, m.p. 48—50 °C. Found (%): C, 55.75; H, 5.42; N, 15.85. $C_{16}H_{18}N_4OS_2$. Calculated (%): C, 55.47; H, 5.24; N, 16.17. IR, ν/cm^{-1}: 3196 (NH), 2956, 2928, 2860 (CH), 2201 (CN), 1608, 1564, 1512, 1440, 1316, 1176, 1140, 1036, 1000, 832, 812, 780, 680. ^{1}H NMR ($CDCl_3$), δ: 0.97 (t, 3 H, CH_3, J = 7.3 Hz); 1.44 (m, 2 H, CH_2); 1.67 (m, 2 H, CH_2); 3.47 (m, 2 H, CH_2); 3.88 (s, 3 H, MeO); 7.00 (d, 2 H, Ar, J = 8.8 Hz); 7.71 (d, 2 H, Ar, J = 8.8 Hz); 8.12 (t, 1 H, NH, J = 4.5 Hz); 8.39 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 13.9 (CH_3); 20.2 (CH_2); 31.6 (CH_2); 42.6 (CH_2); 55.3 (MeO); 116.7 (CN); 114.3 (2 CH, Ar); 128.6 (2 CH, Ar); 110.1; 130.4, 154.9, 161.6, 163.5, 165.0 (6 C_{quat}). MS (EI, 70 eV), m/z (I_{rel} (%)): 346 [M]$^+$ (20), 303 (60), 274 (9), 133 (60), 108 (40).

***N*-Butyl-2-cyano-2-(4-thiophen-2-yl-1,2,3-dithiazol-5-ylidene)ethanimidamide (12d).** The yield was 39%. Yellow crystals, m.p. 57—59 °C. Found (%): C, 48.20; H, 4.57; N, 17.59. $C_{13}H_{14}N_4S_3$. Calculated (%): C, 48.42; H, 4.38; N, 17.37. IR, ν/cm^{-1}: 3268 and 3224 (NH), 3076, 2956, 2928 (CH), 2204 (CN), 1720, 1672, 1532, 1444, 1366, 1292, 1172, 1080, 920, 856, 816, 708. ^{1}H NMR ($CDCl_3$), δ: 0.98 (t, 3 H, CH_3, J = 7.3 Hz); 1.45 (m, 2 H, CH_2); 1.68 (m, 2 H, CH_2); 3.50 (m, 2 H, CH_2); 7.14 (m, 1 H, thienyl); 7.51 (d, 1 H, thienyl, J = 5.1 Hz); 7.65 (d, 1 H, thienyl, J = 3.7 Hz) 8.14 (s, 1 H, NH); 8.45 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 13.8 (CH_3); 20.2 (CH_2); 31.5 (CH_2); 42.5 (CH_2); 125.2 (CN); 126.9, 127.9, and 129.7 (3 CH, thienyl); 116.6; 141.5, 148.8, 153.7, 163.4, 164.4 (6 C_{quat}). MS (EI, 70 eV), m/z (I_{rel} (%)): 332 [M]$^+$ (25), 279 (100), 250 (7), 109 (30), 83 (20).

***N*-Butyl-2-cyano-2-(4-methyl-1,2,3-dithiazol-5-ylidene)-ethanimidamide (11e).** The yield was 52%. Yellow crystals, m.p. 39—41 °C. Found (%): C, 47.50; H, 5.76; N, 21.75. $C_{10}H_{14}N_4S_2$. Calculated (%): C, 47.22; H, 5.55; N, 22.03. IR, ν/cm^{-1}: 3200 (NH), 2952, 2928, 2856 (CH), 2210 (CN), 1696, 1596, 1520, 1456, 1376, 1280, 1180, 1084, 1024, 864, 812, 732, 624. ^{1}H NMR ($CDCl_3$), δ: 0.95 (t, 3 H, CH_3, J = 7.3 Hz); 1.43 (m, 2 H, CH_2); 1.65 (m, 2 H, CH_2); 2.49 (s, 3 H, CH_3); 3.46 (m, 2 H, CH_2); 7.98 (s, 1 H, NH); 8.34 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 13.9 (CH_3); 20.3 (CH_3); 24.3 (CH_2); 31.6 (CH_2); 42.5 (CH_2); 115.8 (CN); 114.1; 153.8; 155.9; 163.6; 164.9 (5 C_{quat}). MS (EI, 70 eV), m/z (I_{rel} (%)): 254 [M]$^+$ (35), 211 (100), 182 (15), 41 (25).

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