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Mechanism of the Zinc-Catalyzed Addition of Azide Ion to Unsaturated Compounds: Synthesis of 5-Substituted 1*H*-Tetrazoles from Nitriles and of 1-Substituted 1*H*-Tetrazole-5-thiols from Isothiocyanates

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Abstract—The mechanism of the formation of 5-substituted 1*H*-tetrazoles from organic nitriles and thiocyanates in the presence of NaN_3 and $ZnCl_2$ in aliphatic alcohols was studied. The results of this study allowed efficient methods of synthesis of substituted tetrazoles from nitriles, thiocyanates, and isothiocyanates to be proposed.

Keywords: 5-substituted 1*H*-tetrazoles, 1-substituted 1*H*-tetrazole-5-thiols, [2+3]-cycloaddition, zinc salts, catalysis

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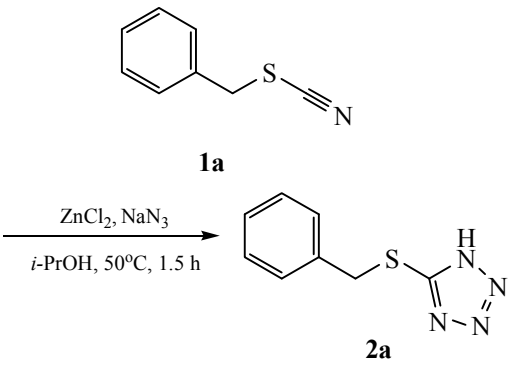
Tetrazoles attract interest which increases with expanding range of practical applications of these compounds. Tetrazole derivatives are widely used as components of pharmaceuticals, energetic materials, gas-generating compositions, and in some other fields [1–3].

At present 5-substituted 1*H*-tetrazoles are synthesized by reactions of hydrazoic acid salts with nitriles and thiocyanates in the presence of various reagents and catalysts like iodine [4], ammonium salts [5], copper [6], and other metals in DMF and scandium [7], bismuth [8], and zinc [9] in water. Lately a lot of papers have been published on the use of recyclable heterogeneous catalysts in the synthesis of tetrazoles [10, 11]. Unfortunately, comparing the reaction conditions in the mentioned and other recent publication we can conclude that no essential progress has been made in the synthesis of tetrazoles, because these methods do not differ much both in reaction temperature and time with the method of synthesis of tetrazoles in the presence of ammonium chloride in DMF developed over 50 years ago [12].

At the same time we previously [13] showed that the catalytic system NaN_3 + $ZnCl_2$ in aliphatic alcohols compares favorably with the catalytic systems commonly used in the synthesis of 5-substituted tetrazoles since it allows successful synthesis at a lower temperature and over a shorter time and, therefore, helps in approaching the problem of the synthesis of tetrazoles from thermally unstable thiocyanates and deactivated aliphatic nitriles. The considerable advantages offered by the system NaN_3 + $ZnCl_2$ in aliphatic alcohols led us to suggest that detailed study of the role of each of its components would make it possible to expand the application field of this system.

First, we studied the kinetic regularities of the process by an example of the model reaction of benzyl thiocyanate (**1a**) with NaN_3 in the presence of $ZnCl_2$ in isopropanol (heterogeneous process) at 50°C (reaction (1)].



1a **2a** (1)

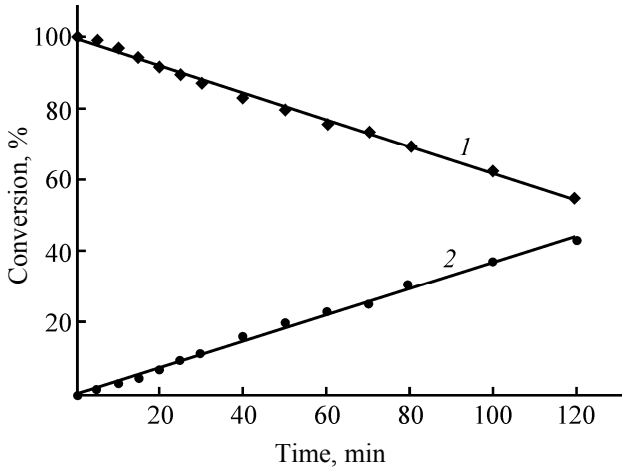


Fig. 1. Kinetic curves of the consumption of (*1*) benzyl thiocyanate and (*2*) accumulation of 5-(benzylsulfanyl)-1*H*-tetrazole in *i*-PrOH at 50°C in the reaction with a 1 : 1 : 1 benzyl thiocyanate : NaN_3 : $ZnCl_2$ molar ratio.

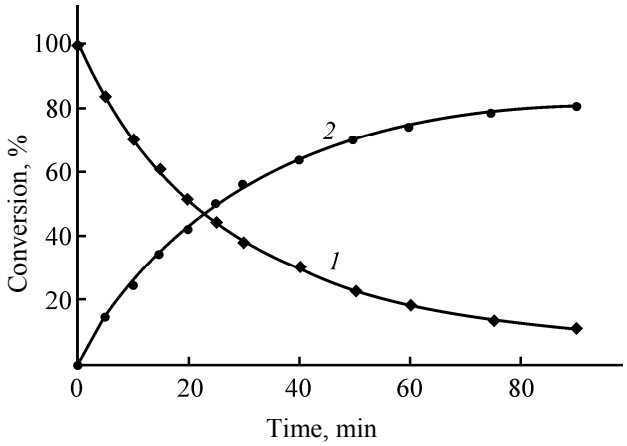


Fig. 2. Kinetic curves of the consumption of (*1*) benzyl thiocyanate and (*2*) accumulation of 5-(benzylsulfanyl)-1*H*-tetrazole in *i*-PrOH at 50°C in the reaction with a 1 : 8 : 8 benzyl thiocyanate : NaN_3 : $ZnCl_2$ molar ratio.

The reaction was performed both with equimolar mounts of reagents and with deficienty of benzyl thiocyanate **1a**. In the first case, the kinetic curves of benzyl thiocyanate **1a** consumption and product **2a** accumulation were linear (Fig. 1). The zero reaction order in thiocyanate shows that the rate of the reagents diffusion to the phase interface is lower than the reaction rate. However, with a 8-fold molar excess of NaN_3 and $ZnCl_2$ with respect to benzyl thiocyanate **1a** both mentioned kinetic curves were no longer linear (Fig. 2). This result suggests a change in the rate-limiting stage: the rate of chemical reaction of compound **1a** becomes lower that the diffusion rate of the reagents to the phase interface. The reaction is now first-order in benzyl thiocyanate.

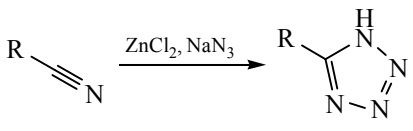
The obtained data show that the limiting stage of the reaction in isopropanol at a 1 : 1 reagent molar ratio involves the formation of a reactive species, and the reaction kinetics depend on the solubility of the reagents. Of all the reaction participants, the least soluble in aliphatic alcohols is NaN_3, and just its dissolution controls the overall reaction rate. The evidence showing that the reaction is diffusion-controlled is provided by the fact that all the 5-substituted sulfanyl-1*H*-tetrazoles obtained in [13], irrespective of the substituent, formed within the same time (1.5 h).

It was found that the reaction of equimolar amounts of NaN_3 and $ZnCl_2$ in isopropanol for 1.5 h at 50°C in the absence of organic thiocyanate formed a precipitate. According to the results of argentometric titration, this precipitate was a 95% NaCl. Complexometric titration showed that more than 90% of Zn used in the reaction was present in the solution.

Thus, the rate-limiting stage of the synthesis of tetrazoles in isopropanol is the reaction of $ZnCl_2$ and NaN_3 to form NaCl and a reactive intermediate, specifically, the mixed zinc salt $ZnClN_3$, and the latter enters cycloaddition with nitrile or thiocyanate [reaction (2)].

$$ZnCl_2 + NaN_3 \xrightarrow[50^oC,\ 1.5\ h]{i\text{-PrOH}} ZnClN_3 + NaCl\downarrow. \qquad (2)$$

Further on we studied the kinetics of the model reaction in ethylene glycol. The latter solvent provides homogeneity of the system over the entire process. The kinetic curves for the reaction of $ZnCl_2$, NaN_3, and benzyl thiocyanate in ethylene glycol are presented in Figs. 3 and 4. The calculated partial reaction order in benzyl thiocyanate was 1 both with deficienty of thiocyanate and with equimolar amounts of the reagents, implying that this reaction is not diffusion-controlled. It was found that the rates of formation of 5-substituted 1*H*-tetrazoles from compounds **1a–1f** in ethylene glycol were higher compared to the heterogeneous process, but the yields of the reaction products in the two processes were comparable [reaction (3), see the table].



1a–1f **2a–2f** (3)

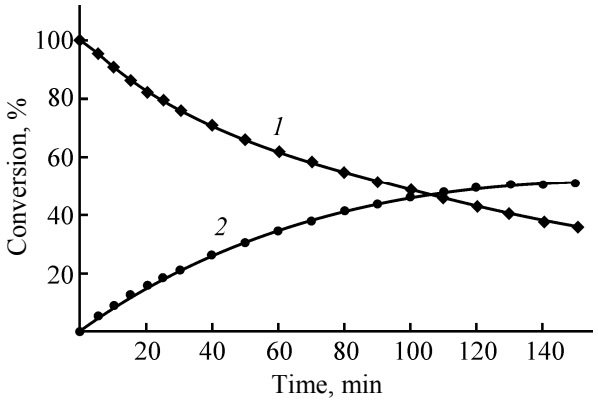


Fig. 3. Kinetic curves of the consumption of (*1*) benzyl thiocyanate and (*2*) accumulation of 5-(benzylsulfanyl)-1*H*-tetrazole in ethylene glycol at 50°C in the reaction with a 1 : 1 : 1 benzyl thiocyanate : NaN_3 : $ZnCl_2$ molar ratio.

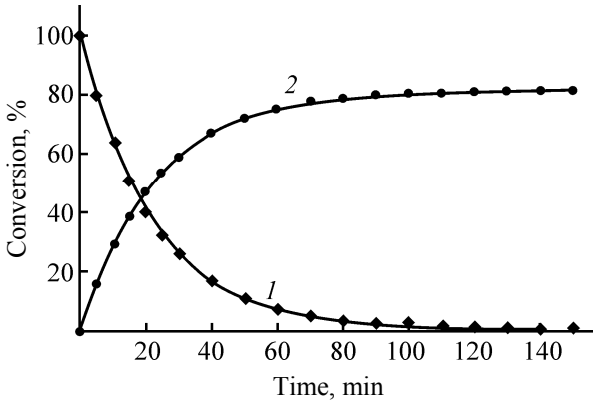


Fig. 4. Kinetic curves of the consumption of (*1*) benzyl thiocyanate and (*2*) accumulation of 5-(benzylsulfanyl)-1*H*-tetrazole in ethylene glycol at 50°C in the reaction with a 1 : 8 : 8 benzyl thiocyanate : NaN_3 : $ZnCl_2$ molar ratio.

It should be noted that in the synthesis of tetrazoles from deactivated nitriles (compound **1f**), which is a rather long process, the fact that the reaction rate is no longer controlled by diffusion does not have such a strong accelerating effect.

Earlier we showed [13] that the yield of 5-substituted 1*H*-tetrazoles depended on the nature of the alcohol: the yields both in the sterically compact MeOH and in the sterically bulky *tert*-butanol proved to be much lower than in ethanol, isopropanol, *n*-propanol, and *n*-butanol. Therewith, the solvents traditionally used in tetrazole synthesis (DMSO, DMF, MeCN, H_2O) were inefficient at such a low temperature.

The above findings suggest that alcohol in the synthesis of 5-substituted 1*H*-tetrazoles acts not only as a solvent but also as a reagent. As known, organic nitriles can react with alcohols to form imino ethers. We assumed that in our case zinc compounds present in the reaction mixture favor the formation of an imino ether intermediate [reaction (4)].

$$R^1-C\equiv N: \longleftrightarrow R^1-\overset{+}{C}=\overset{-}{N}:$$

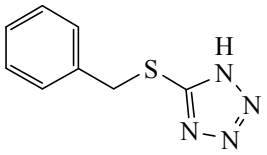
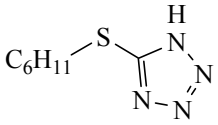
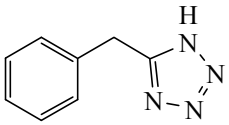
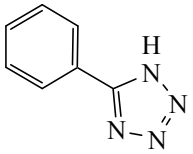
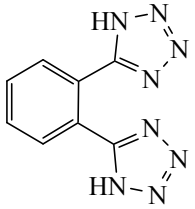
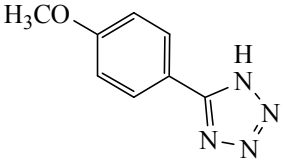
$$\xrightarrow[50^\circ C]{R^2OH,\ ZnClN_3} R^1-C(=NH)-O-R^2 \qquad (4)$$

Under these conditions the lower efficiency of the reaction in methanol is due to the high stability of the imino ether intermediate, which originates from the comparable nucleophilicity of the methoxy group and azide ion. In the case of *tert*-butanol, the yield of the product decreased by steric reasons.

However, we could not obtain any experimental evidence for the formation of imino ethers, and therefore, to substantiate this hypothesis, therefore we performed quantum-chemical calculations using the example of acetonitrile. It was found that the limiting stage of the formation of 5-substituted 1*H*-tetrazole from acetonitrile and $ZnClN_3$ is the nucleophilic substitution of the ether group in the imino ether intermediate by the azido group to form an imidoyl azide intermediate with the activation energy of 45.24 kJ/mol. At the same time in the absence of Lewis acid, when alcohol does not add to unactivated nitrile, the limiting stage of the formation of 5-substituted 1*H*-tetrazole from MeCN and NaN_3 is the addition of the azide ion to nitrile to form an imidoyl azide intermediate with the activation barrier of 96.19 kJ/mol.

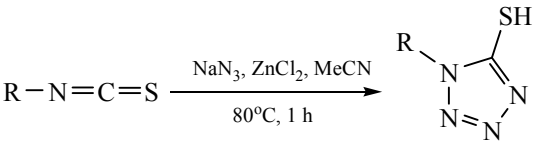
In summary, the obtained data allow us a suggestion of the following mechanism of the [2+3]-cycloaddition of NaN_3 to organic nitriles and thiocyanates in the presence of $ZnCl_2$ in aliphatic alcohols (Scheme 1). The mixed zinc salt $ZnClN_3$ formed *in situ* in the reaction of NaN_3 and $ZnCl_2$ acts both as a source of azide ions and as a Lewis acid. The latter favors polarization of the CN bond, resulting in the alcohol addition to nitrile to form the intermediate imino ether. Further on, the intermediate reacts with azide ion to form the intermediate imidoyl azide, because the energy barrier for the nucleophilic substitution of the ether by azido group is much lower than for the addition of the azide ion to a unactivated nitrile. The resulting imidoyl azide intermediate undergoes cyclization to form zinc salt of 5-substituted 1*H*-tetrazole, which is then decomposed with alkali and acidified to isolate the target product.

Synthesis of 5-substituted 1*H*-tetrazoles in heterogeneous (monoatomic aliphatic alcohols) and homogeneous (ethylene glycol) conditions

Comp. no.	Tetrazole	*T*, °C	Time, h	
			ROH [13]	$HO(CH_2)_2OH$
1a		50	1,5 (*i*-PrOH)	0.50
1b		50	1,5 (*i*-PrOH)	0.25
1c		95	2 (*p*-PrOH)	1.00
1d		95	1 (*p*-PrOH)	0.67
1e		95	1 (*p*-PrOH)	0.33
1f		95	7 (*p*-PrOH)	7.00

We suggested that the *in situ* formation of the reactive mixed zinc salt $ZnClN_3$ could also drive other cycloaddition reactions. Among the most common cycloaddition reactions of inorganic azides an important role belongs to the synthesis of 1-substituted 1*H*-tetrazole-5-thiols from organic isothiocyanates, which usually requires prolonged boiling in water [14].

Indeed, aromatic and aliphatic isocyanates **3a–3f** reacted with NaN_3 in the presence of $ZnCl_2$ in MeCN to form 1-substituted 1*H*-tetrazole-5-thiols **4a–4f** within a short time at a fairly low temperature [reaction (5)].



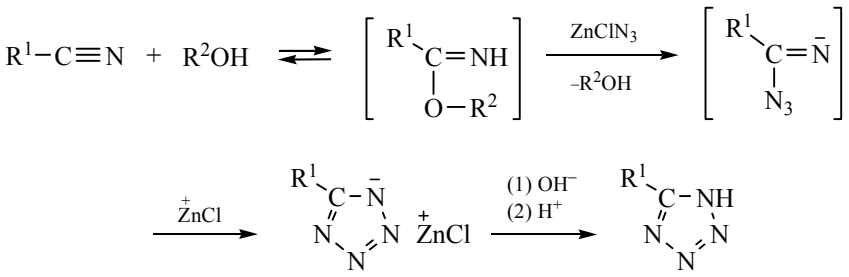
(5)

3a–**3f** **4a**–**4f** (65–99%)

R = allyl (**a**), $PhCH_2$ (**b**), Ph (**c**), $(2\text{-}COOMe)C_6H_4$ (**d**), $(2\text{-}F_2HCO)C_6H_4$ (**e**), 1-naphthyl (**f**).

The yields of tetrazole-5-thiols in aliphatic alcohols proved to be lower than in MeCN, probably, because of *O*-thiocarbamate formation. It should be noted that

Scheme 1.



in the absence of $ZnCl_2$ no formation of 1-substituted 1*H*-tetrazole-5-thiols from isothiocyanates in MeCN was observed.

Thus, the key stage that controls the cycloaddition of the azide ion to nitriles (thiocyanates) and isothiocyanates is the *in situ* formation of the mixed salt $ZnClN_3$. The use of the NaN_3–$ZnCl_2$ system much decreases the time and temperature of the synthesis of 1-substituted 1*H*-tetrazole-5-thiols from isothiocyanates. In the case of nitriles, the formation of the intermediate imino ether additionally decreases the activation energy, which, together with the fact that the reaction in ethylene glycol is no longer diffusion-controlled, allows us to consider the proposed procedure as the presently most efficient synthetic approach to 5-substituted 1*H*-tetrazoles.

EXPERIMENTAL

The IR spectra were registered on a Shimadzu FTIR-8400S spectrometer in KBr pellets. The ^1H and ^{13}C NMR spectra were obtained on a JEOL JNM-ECX 400A spectrometer (400 and 100 MHz, respectively) in DMSO-d_6, internal reference residual proton signals of the solvent. Elemental analysis was performed on a LECO CHNS-932 analyzer. The melting points were measured on a Koeffler heating block. The purity and individuality of the synthesized compounds were controlled by TLC on Silufol UV-254 plates.

5-(Benzylsulfanyl)-1*H*-tetrazole (2a). Sodium azide, 0.52 g (8.0 mmol), and 1.10 g (8.0 mmol) of $ZnCl_2$ were added to 30 mL of ethylene glycol. The mixture was heated with stirring at 50°C, after which 1 g (6.7 mmol) of benzyl thiocyanate was added. The reaction mixture was stirred for 0.5 h, and the solvent was then removed in a vacuum. The residue was treated with 5% aqueous NaOH (50 mL) with stirring for 20 min, and the resulting suspension was filtered. The aqueous layer was acidified with conc. HCl to pH 1. The precipitate that formed was filtered off, washed with water, and dried in air. Yield 1.17 g (91%), colorless crystals, mp 135–137°C (EtOH) (mp 134–135°C [15]). IR spectrum, ν, cm^{-1}: 2895 (CH_2), 1532 (C=N), 1454 (Ph), 1079 (C–N), 704 (C–S). ^1H NMR spectrum, δ, ppm: 4.47 s (2H, CH_2), 7.20–7.28 m (3H, H-Ar), 7.35–7.37 m (2H, H-Ar). ^{13}C NMR spectrum, δ_C, ppm: 36.51 (CH_2), 128.20 (Ph), 129.09 (Ph), 129.45 (Ph), 137.22 (Ph), 154.23 (C–N). Found, %: C 49.87; H 4.35; N 29.00; S 16.79. $C_8H_8N_4S$. Calculated, %: C 49.98; H 4.19; N 29.14; S 16.68.

Compounds **2b–2f** were prepared in a similar way.

5-(Hexylsulfanyl)-1*H*-tetrazole (2b). Yield 1.03 g (79%), colorless crystals, mp 85–87°C (CCl_4) (mp 85°C [15]). IR spectrum, ν, cm^{-1}: 2948 (CH_3), 2857 (CH_2), 1522 (C=N), 1041 (C–N), 718 (C–S). ^1H NMR spectrum, δ, ppm: 0.80 t (3H, CH_3, J = 12.0 Hz), 1.18–1.22 m (4H, CH_2CH_2), 1.28–1.36 m (2H, CH_2), 1.58–1.65 m (2H, CH_2), 3.18 t (2H, CH_2, J = 12.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.35 (CH_3), 22.47 (CH_2), 28.02 (CH_2), 29.54 (CH_2), 31.15 (CH_2), 32.46 (CH_2), 154.63 (C–N). Calculated, %: C 45.13; H 7.58; N 30.08; S 17.21. $C_7H_{14}N_4S$. Found, %: C 45.01; H 7.50; N 29.99; S 17.06.

5-Benzyl-1*H*-tetrazole (2c). Yield 1.14 g (83%), colorless crystals, mp 123–124°C (EtOAc) (mp 123–124°C [16]). IR spectrum, ν, cm^{-1}: 2852 (CH_2), 1596 (C=N), 1494 (Ph), 1176 (C–N). ^1H NMR spectrum, δ, ppm: 4.26 s (2H, CH_2), 7.20–7.32 m (5H, H-Ar), 16.18 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 29.43 (CH_2), 127.55 (Ph), 128.67 (Ph), 129.19 (Ph), 136.45 (Ph), 155.77 (C–N). Found, %: C 60.14; H 5.17; N 35.05. $C_8H_8N_4$. Calculated, %: C 59.99; H 5.03; N 34.98.

5-Phenyl-1*H*-tetrazole (2d). Yield 1.18 g (83%), colorless crystals, mp 214–216°C (EtOAc) (mp 215–216°C [9]). IR spectrum, ν, cm^{-1}: 1564 (C=N), 1483 (Ph), 1163 (C–N). ^1H NMR spectrum, δ, ppm: 7.49–7.50 m (3H, H-Ar), 7.98–8.00 m (2H, H-Ar), 15.78 s

(1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 124.67 (Ph), 127.47 (Ph), 129.82 (Ph), 131.63 (Ph), 155.81 (C–N). Found, %: C 57.42; H 4.19; N 38.23. $C_7H_6N_4$. Calculated, %: C 57.53; H 4.14; N 38.34.

5,5'-Benzene-1,2-diylbis(1*H*-tetrazole) (2e). Yield 1.54 g (92%), colorless crystals, mp 230–232°C (EtOH) (mp 228–230°C [9]). IR spectrum, ν, cm^{-1}: 1546 (C=N), 1469 (Ph), 1064 (C–N). ^{1}H NMR spectrum, δ, ppm: 7.74–7.78 m (2H, H-Ar), 7.88–7.92 m (2H, H-Ar). ^{13}C NMR spectrum, δ_C, ppm: 125.03 (Ar), 131.32 (Ar), 131.82 (Ar), 155.24 (C–N). Found, %: C 45.02, H 2.77; N 52.39. $C_8H_6N_8$. Calculated, %: C 44.86; H 2.82 N 52.32.

5-(4-Methoxyphenyl)-1*H*-tetrazole (2e). Yield 1.21 g (91%), colorless crystals, mp 232–234°C (EtOAc) (231–232°C [9]). IR spectrum, ν, cm^{-1}: 2984 (CH_3), 1501 (C=N), 1443 (Ph), 1265 (C–O–C=), 1183 (C–N). ^{1}H NMR spectrum, δ, ppm: 3.77 s (3H, CH_3), 7.08 d (2H, H-Ar, J = 4.0 Hz), 7.93 d (2H, H-Ar, J = 12.0 Hz), 16.47 s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 55.88 (CH_3), 115.27 (Ar), 116.79 (Ar), 129.13 (Ar), 155.24 (C–N), 161.95 (C–O). Found, %: C 54.50; H 4.57; N 31.82. $C_8H_8N_4O$. Calculated, %: C 54.59; H 4.66; N 31.89.

1-Allyl-1*H*-tetrazole-5-thiol (4a). Sodium azide, 0.79 g (12.1 mmol), and 1.65 g (12.1 mmol) of $ZnCl_2$. were added to 30 mL of MeCN. The mixture was heated with stirring until boiling (80°C), and then 1 g (10.1 mmol) of allyl isothiocyanate was added. The reaction mixture was stirred for 1 h at 80°C, and the solvent was then removed in a vacuum. The residue was treated with 5% aqueous NaOH (50 mL) with stirring for 20 min. The suspension was filtered, and the filtrate was treated with chloroform (2×10 mL) to remove impurities. The aqueous layer was acidified with conc. HCl to pH 1. The precipitate that formed was filtered off, washed with water, and dried in air. Yield 0.97 g (68%), yellowish crystals, mp 67–69°C (EtOH) (mp 69°C[14]). IR spectrum, ν, cm^{-1}: 2937 (CH_2), 2560 (SH), 1645 (C=C), 1504 (C=N), 1182 (C–N), 741 (C–S). NMR spectrum ^{1}H, δ, ppm: 4.78 d (2H, CH_2, J = 8.0 Hz), 5.25 d (2H, CH_2, J = 12.0), 5.87–5.97 m (1H, CH). NMR spectrum ^{13}C, δ_C, ppm: 48.7 (CH_2), 119.9 (CH_2), 130.5 (CH), 164.5 (C–S). Found, %: C 33.60; H 4.41; N 39.49; S 22.43. $C_4H_6N_4S$. Calculated, %: C 33.79; H 4.25; N 39.40; S 22.55.

Compounds **4b–4f** were prepared in a similar way.

1-Benzyl-1*H*-tetrazole-5-thiol (4b). Yield 0.84 g (65%), colorless crystals, mp 142–144°C (H_2O) (mp 144°C [14]). IR spectrum, ν, cm^{-1}: 2930 (CH_2), 2556 (SH), 1504 (C=N), 1452 (Ph), 1183 (C–N), 708 (C–S). ^{1}H NMR spectrum, δ, ppm: 5.38 s (2H, CH_2), 7.24–7.30 m (3H, H-Ph), 7.36–7.38 m (2H, H-Ph). ^{13}C NMR spectrum, δ_C, ppm: 49.7 (CH_2), 128.3 (Ph), 128.7 (Ph), 129.1 (Ph), 134.8 (Ph), 164.8 (C–S). Found, %: C 50.08; H 4.02; N 29.07; S 16.82. $C_8H_8N_4S$. Calculated, %: C 49.98; H 4.19; N 29.14; S 16.68.

1-Phenyl-1*H*-tetrazole-5-thiol (4c). Yield 1.31 g (99%), colorless crystals, mp 148–150°C (H_2O) (mp 150°C [14]). IR spectrum, ν, cm^{-1}: 2549 (SH), 1510 (C=N), 1457 (Ph), 1153 (C–N), 725 (C–S). ^{1}H NMR spectrum, δ, ppm: 7.44–7.54 m (3H, H-Ph), 7.89–7.92 m (2H, H-Ph). ^{13}C NMR spectrum, δ_C, ppm: 124.0 (Ph), 129.3 (Ph), 134.8 (Ph), 164.1 (C–S). Found, %: C 47.29; H 3.50; N 31.56; S 18.11. $C_7H_6N_4S$. Calculated, %: C 47.18; H 3.39; N 31.44; S 17.99.

Methyl 2-(5-mercapto-1*H*-tetrazol-1-yl)benzoate (4d). Yield 0.76 g (62%), colorless crystals, mp 144–146°C (EtOH). IR spectrum, ν, cm^{-1}: 2913 (CH_3), 2566 (SH), 1719 (COO), 1601 (C=N), 1491 (Ar), 1191 (C–N), 703 (C–S). ^{1}H NMR spectrum, δ, ppm: 3.70 s (3H, CH_3), 7.56 d (1H, H-Ar, J = 8.0 Hz), 7.69 t (1H, H-Ar, J = 16.0 Hz), 7.79 t (1H, H-Ar, J = 16.0 Hz), 8.05 d (1H, H-Ar, J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 52.8 (CH_3), 128.3 (C Ar), 129.3 (Ar), 131.1 (Ar), 131.6 (Ar), 132.4 (Ar), 133.7 (Ar), 164.4 (C–S), 167.3 (C=O). Found, %: C 45.61; H 3.58; N 23.79; S 13.40. $C_9H_8N_4O_2S$. Calculated, %: C 45.75; H 3.41; N 23.72; S 13.57.

1-[2-(Difluoromethoxy)phenyl]-1*H*-tetrazole-5-thiol (4e). Yield 0.98 g (81%), colorless crystals, mp 134–136°C (EtOH). IR spectrum, ν, cm^{-1}: 2927 (CH), 2561 (SH), 1605 (C=N), 1492 (Ar), 1281 (=C–O–C), 1181 (C–N), 1054 (CF_2), 721 (C–S). ^{1}H NMR spectrum, δ, ppm: 6.97 t (1H, CHF_2, J = 12.0 Hz), 7.39–7.44 m (2H, H-Ar), 7.54–7.62 m (2H, H-Ar). ^{13}C NMR spectrum, δ_C, ppm: 113.8 (Ar), 116.4 (Ar), 120.1 (Ar), 125.9 (Ar), 130.1 (Ar), 147.1 (Ar), 164.4 (C–S), 167.3 (CHF_2). Found, %: C 39.21; H 2.59; N 23.11; S 13.01. $C_8H_6F_2N_4OS$. Calculated, %: C 39.34; H 2.48; N 22.94; S 13.13.

1-(Naphthalen-1-yl)-1*H*-tetrazole-5-thiol (4f). Yield 0.97 g (79%), colorless crystals, mp 146–148°C (EtOH). IR spectrum, ν, cm^{-1}: 2553 (SH), 1504 (C=N), 1466 (Ar), 1183 (C–N), 727 (C–S). ^{1}H NMR spectrum, δ, ppm: 7.39 d (1H, H-Ar, J = 8.0 Hz), 7.51–7.57 m

(2H, H-Ar), 7.63–7.67 m (2H, H-Ar), 8.00 d (1H, H-Ar, J = 8.0 Hz), 8.09–8.11 m (1H, H-Ar). ^{13}C NMR spectrum, δ_C, ppm: 122.8 (Ar), 125.5 (Ar), 126.3 (Ar), 126.7 (Ar), 127.2 (Ar), 128.8 (Ar), 129.2 (Ar), 130.3 (Ar), 131.5 (Ar), 134.4 (Ar), 164.4 (C–S). Found, %: C 57.70; H 3.72; N 24.68; S 14.15. $C_{11}H_8N_4S$. Calculated, %: C 57.88; H 3.53; N 24.54; S 14.05.

Kinetic measurements were performed on a Shimadzu Prominence LC-20 chromatograph with diode array, column Luna 5μm C18(2)100A 250×3 mm, eluent MeCN–[90% H_2O (pH 3, H_3PO_4) + 10% MeCN], 65:35; column temperature 35°C, flow rate 0.4 mL/min, λ 243 nm.

Two series of model reactions were used for kinetic measurements, one in isopropanol (heterogeneous process) and the other in ethylene glycol (homogeneous process). The reactions were performed at 50°C under the following conditions:

– reaction in isopropanol with equimolar amounts of the reagents: benzyl thiocyanate 0.10 g (0.67 mmol), NaN_3 0.04 g (0.67 mmol), $ZnCl_2$ 0.09 g (0.67 mmol), isopropanol 10 mL;

– reaction in isopropanol with a 8-fold molar excess of NaN_3 and $ZnCl_2$ with respect to benzyl thiocyanate: benzyl thiocyanate 0.10 g (0.67 mmol), NaN_3 0.34 g (5.37 mmol), $ZnCl_2$ 0.73 g (5.37 mmol), isopropanol 10 mL;

– reaction in ethylene glycol with equimolar amounts of the reagents: benzyl thiocyanate 0.20 g (1.34 mmol), NaN_3 0.08 g (1.34 mmol), $ZnCl_2$ 0.18 g (1.34 mmol), ethylene glycol 10 mL;

– reaction in ethylene glycol with a 8-fold molar excess of NaN_3 and $ZnCl_2$ with respect to benzyl thiocyanate: benzyl thiocyanate 0.20 g (1.34 mmol), NaN_3 0.69 g (10.73 mmol), $ZnCl_2$ 1.46 g (10.73 mmol), ethylene glycol 10 mL.

Sample preparation for the reaction in isopropanol. Sodium azide was added to a hot (50°C) solution of benzyl thiocyanate and $ZnCl_2$ in isopropanol. This moment was taken for the reaction start time. After a definite time interval, the reaction mixture was transferred to a 250-mL measuring flask and diluted, its volume was adjusted to the mark with a solution containing H_2O (pH 3, H_3PO_4) and *i*-PrOH (1 : 1); as a result, the precipitate dissolved completely. The resulting solution was heated at 50°C. Samples for HPLC analysis were taken in 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 100, and 120 min after start of heating (for the reaction with a 1 : 1 : 1 benzyl thiocyanate : NaN_3 : $ZnCl_2$ molar ratio) and in 5, 10, 15, 20, 25, 30, 40, 50, 60, 75, and 90 min (for the reaction with a 1 : 8 : 8 benzyl thiocyanate : NaN_3 : $ZnCl_2$ molar ratio).

Sample preparation for the reaction in ethylene glycol. Sodium azide was added to a hot (50°C) solution of benzyl thiocyanate and $ZnCl_2$ in ethylene glycol. This moment was taken as the reaction start time. In definite time intervals, 25-μL samples were taken from the reaction mixture and diluted with 2 mL of a solution containing H_2O (pH 3, H_3PO_4) and *i*-PrOH (1 : 1). Aliquots of the resulting solution were analyzed by HPLC.

Quantum-chemical calculations were performed using GAMESS (developer the Quantum Chemistry Group, Iowa State University, http://www.msg.chem.iastate.edu/gamess/index.html). The enthalpies of formation were obtained by the DFT B3LYP/6-31G calculations. Solvent (ethanol) effects were included by the PCM method. The calculated energies were corrected for zero-point vibrational energies.

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