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SYNTHESIS OF 2-AZIDO-1,3-THIAZOLES AS 1,2,3-TRIAZOLE PRECURSORS

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By diazotization of 2-aminothiazoles and reaction with sodium azide, the derivatives of 2-azidothiazole were synthesized. Conditions of diazotization were selected according to the nature of a substituent in thiazoles. 2-Azidothiazole derivatives were studied in the base-catalysed condensation reactions with activated methylenic compounds to yield new 1-(1,3-thiazol-2-yl)-1H-1,2,3-triazole-4-carboxylic acids.

Keywords: Azides; cyclocondensation; thiazoles; 1,2,3-triazoles

Azides are convenient reagents for the synthesis of triazoles,[1–5] which are widely used for medical and technical purposes.[4,5] The reaction of diazonium salts with sodium azides is one of the synthetic paths for aromatic azide preparation. The reaction takes place without any catalysts with the formation of azides in good yields.[1] The diversity of available aromatic amines is the advantage of such a method. However, heterocyclic azides, yielded from the corresponding amines, are poorly described in literature because of the insufficient study of heterocyclic diazonium salts.[6]

In the current article, some 2-amino-1,3-thiazoles, which are easily prepared by Hantzsch cyclization from α-halocarbonylic compounds and thiourea, were studied as starting reagents for 2-azido-1,3-thiazoles. Unfortunately, there are not many examples of this class of compounds studied in the diazotization reaction because of the structural peculiarities of 2-amino-1,3-thiazoles. One of the major problems of the amino group reactivity in 2-amino-1,3-thiazoles is a tautomeric equilibrium (Fig. 1). Literary data analysis in relation to the tautomeric equilibrium of 2-imino(amino)-thiazoline derivatives shows that predominance of the tautomeric form depends on the aggregate state and, in solutions, on the nature of solvent.[7]

Commercially available α-halogencarbonyl compounds, as starting materials, were used for the synthesis of 2-aminothiazoles **2a**–**e**. However, the method described in Ref. 8[8] was used for the preparation of compounds **2f**–**i**. 3-Aryl-2-chloropropanals **1f**–**i** were prepared by the reaction of arenediazonium chlorides with acrolein under conditions of the Meerwein reaction (Scheme 1).

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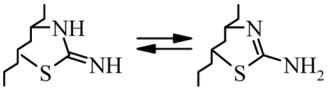


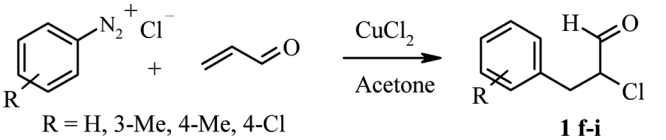
Figure 1. Tautomeric equilibrium.

α-Haloaldehydes **1f–i** or α-haloketones reacted with thiourea and formed 2-amino-1,3-thiazoles **2a–i** with good yields (Scheme 2).[8]

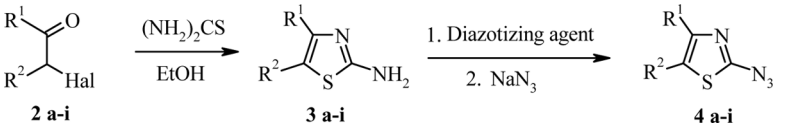
Herein we describe novel advantages of 2-aminothiazole derivative diazotization. Three types of diazotization reagents [nitrosyl chloride ($NaNO_2$ in HCI solution), nitrosylsulfuric acid ($NaNO_2$, in H_2SO_4 either 40% or 70% solutions), and nitrosylnitric acid ($NaNO_2$ in the mixture HNO_3–H_3PO_4)] were used for diazotization.

We have succeeded in diazotization of 2-aminothiazole in concentrated HCl and synthesized azide **4a** with 36% yield.[9] Unfortunately, some quantity of the 2-aminothiazole remained unreacted after diazotization. Furthermore, only 2-aminothiazole formed diazonium salt in concentrated HCl. In case of the other 2-aminothiazoles, efficient diazotization can be achieved only by using nitrosylsulfuric acid obtained from $NaNO_2$ and concentrated H_2SO_4 (Table 1). Yield of diazonium salts in diazotization reaction of substituted 2-aminothiazoles depended on the character of the substituent and reaction conditions. 1,3-Thiazol-2-amines **2b,c** and **2f–i** reacted with nitrosyl ion in sulfuric acid. However, diazotization in nitrosylsulfuric acid occurred very slowly because the concentration of the free amine was exceedingly low. 4-Aryl-1,3-thiazol-2-amines **3d,e** formed diazonium salt only in the mixture of phosphoric and nitrate acids. Compounds **4d,e** were formed by treatment of diazonium salt solution with sodium azides. Previously, compounds **4a,d,e** were prepared by the reaction of sodium azide with 2-diazonium salts of 2-aminothiazole in sulfuric acid with approximately 15% yields.[9] A particular nitrosyl agent ($NaNO_2$ in HNO_3–H_3PO_4 solution) was used as an extensive diazotizing agent for weakly basic amines. Thus, 2-azido-1,3-thiazoles **4a–i** were synthesized under optimal conditions selected for diazotization of amines **3a–i** (Tables 1 and 2).

It is well known that thiazoles and other nitrogen-bearing heterocycles[10] (including the azido group in the α-position of nitrogen in the cycle), depending



Scheme 1. Synthesis of 3-aryl-2-chloropropanals **1f–i**.



Scheme 2. Synthesis of 2-azido-1,3-thiazoles **4a–i**.

Table 1. Synthesis of azides **4a–i**

Compound	R^1	R^2	Condition of diazotization of amines **3** and yield[a] (%) of azides **4**			
			HCl conc.	H_2SO_4 (≈40%)	H_2SO_4 (≈70%)	$H_3PO_4 + HNO_3^c$
4a	H	H	36	—	—	20
4b		$-(CH_2)_4-$	—[b]	41	68	
4c	Me	COOEt	—	—	71	
4d	Ph	H	—	—	—	23
4e	4-MeC_6H_4	H	—	—	—	29
4f	H	$PhCH_2$	—	21	52	
4g	H	3-$MeC_6H_4CH_2$	—	—	41	
4h	H	4-$MeC_6H_4CH_2$	—	—	56	
4i	H	4-$ClC_6H_4CH_2$	—	14	43	

[a]Isolated yields are based on single experiment and the yields were not optimized.
[b]No reaction.
[c]Mixture of H_3PO_4 (80%) and concentrated HNO_3 (2.2:1 by volume).

on the aggregate state and polarity of solvent, can exist in either azido and tetrazole forms or in the state of azido-tetrazole equilibrium. Tautomerizme of azides **4** were studied.[9,11,12]

Such a tautomerizme is increasingly investigated by quantum chemical methods. The transformation of 2-azidothiazole **4a** into thiazolo[3,2-*d*]tetrazole **4a′** has been studied as a prototype reaction for the generation of tetrazoles (Fig. 2).[13,14]

In the infrared (IR) spectra of compounds **4a–i** in CCl_4 solutions, intensive azide bands are present in regions 2130–2265 cm^{-1} (νN_3). These bands are most intensive in the IR spectra, which proves the predominance of azido form in these compounds.

Thus, the results of the spectral research show that studied compounds in solutions exist mainly in azido form. It made it possible to use them in the characteristic

Table 2. Azides **4a–i**

Compound	MS (CI) *m/z*	Temp. (°C)[a]	IR[b] [$\nu(N_3)$ cm^{-1}]
4a	126	—	2135
4b	180	109–110	2138
4c	212	39–40	2162
4d	202	87–88	2137
4e	216	62–63	2140
4f	216	57–56	2144
4g	230	—	2145
4h	230	64–65	2140
4i	251	91–92	2144

[a]All melting points are given for crude products without purification and are uncorrected.
[b]IR spectra were recorded in CCl_4 solution.

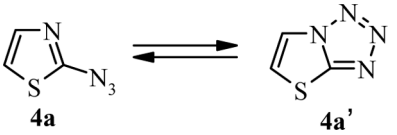


Figure 2. Azido-tetrazole equilibrium.

reactions of azides for triazole synthesis. For instance, 2-azido-1,3-thiazole, prepared from 1,3-thiazolelithium and tosyl azide by the azido transfer procedure, was used for the synthesis of 1–1,3-thiazole-4-trimethylsilyl-1,2,3-triazole by 1,3-dipolar cycloaddition.[15]

One of the most convenient methods of triazole synthesis is the base-catalyzed cyclization of organic azides with CH acids (Dimroth cyclization).[4] The reaction occurred at different rates depending on the dipolarophile. However, in some cases (especially when azides were used with an electron-withdrawing substituent), reduction of the azido moiety to the amino group took place instead of the triazole formation.[4]

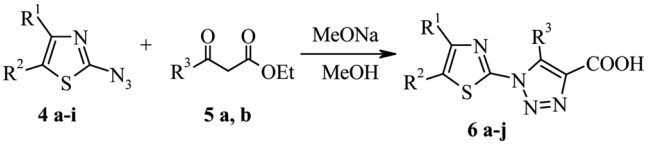
Previously, only two 2-azidothiazole derivatives were studied in such reactions.[12] Thus, to explore the synthetic application of azides **4** for triazole synthesis, we have carried out some cylocondensation reactions with β-ketoesters.

It was established that base-catalyzed reactions of azides **4** with ethyl acetoacetate and ethyl benzoylacetate **5b** occurred at room temperature. Completion of the reaction was defined with disappearance of the absorption band of azido moiety in IR spectrum of the reaction mixture. During the reaction, we observed exclusive formation of triazoles **6** (Table 3). Moreover, the electron-poor 2-azidothiazoles rapidly reacted and were converted into products in good yield.

In conclusion, 2-azidothiazoles were synthesized by diazotization of 2-aminothiazoles and subsequent treatment with sodium azides. Conditions of diazotization were optimized according to the character of a substituent. This method can be an excellent synthetic route to new (1,3-thiazol-2-yl)-1*H*-1,2,3-triazoles.

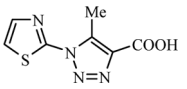
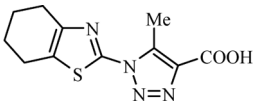
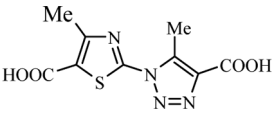
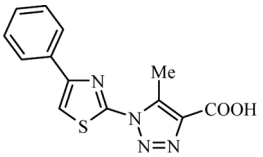
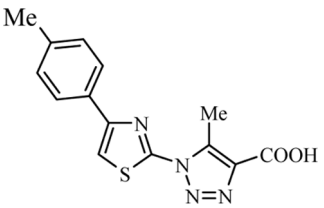
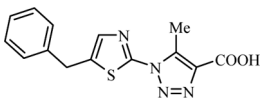
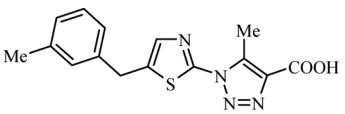
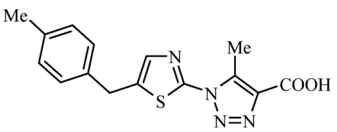
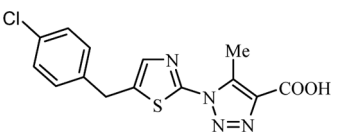
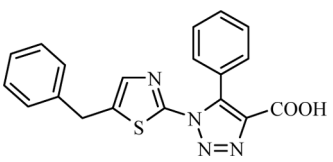
EXPERIMENTAL

^{1}H NMR spectra were recorded on a Varian Mercury 400 instrument (400 MHz for ^{1}H). The ^{1}H chemical shifts were reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal reference. Mass spectra (MS) were run using Agilent 1100 series liquid chromatography (LC)/MS instrument with atmospheric pressure ionization–electrospray/atmospheric pressure chemical ionization (API-ES/APCI) mode. 2-Aminothiazoles **3b–e** were prepared



Scheme 3. Synthesis of (1,3-thiazol-2-yl)-1*H*-1,2,3-triazoles **6a–j**.

Table 3. 1-(1,3-Thiazol-2-yl)-1*H*-1,2,3-triazole-4-carboxylic acids **6a**–**h**

Compound	Product	Yield (%)
6a		42
6b		71
6c		64
6d		79
6e		82
6f		75
6g		71
6h		83
6i		87
6j		79

from the commercially available α-haloketones, their constants are described in the literature.[7]

Synthesis of 2-Azido-1,3-thiazole 4a

2-Amino-1,3-thiazole **3a** (0.05 mol) was dissolved in concentrated HCl (19 mL). The solution was cooled to 0°C, and sodium nitrite (3.45 g, 0.05 mol) in a minimal quantity of water was added dropwise while keeping the temperature below 5°C. The solution of sodium azide (3.25 g, 0.05 mol) in 10 mL of water was added slowly with intensive stirring. The temperature was kept below 7°C. After sodium azide was added, the mixture was left for 2 h at room temperature, and azide was extracted by diethyl ether (3 × 10 mL). Ether was evaporated in vacuo. Azide **4a** was used without subsequent purification (mp 94°C, lit.[15] 94–96°C).

Synthesis of 2-Azido-1,3-thiazoles 4b,c,f–i

An appropriate 2-amino-5-(R-benzyl)-1,3-thiazole **3b,c,f–i** (0.02 mol) was dissolved in the mixture of concentrated sulfuric acid (5 mL) and water (5 mL). When the mixture was cooled to 0°C, saturated sodium nitrite (1.73 g; 0.025 mol) aqueous solution was added while keeping the temperature below 5°C. After 10 min, resinous sediment (if it was formed) was filtered. To the filtrate solution of the diazonium salt, sodium azide (1.3 g; 0.02 mol) in 5 mL of water was added dropwise. The solution was left for 15 min at room temperature, and azide was extracted by diethyl ether (3 × 15 mL). Azides were used without the subsequent purification.

Synthesis of 2-Azido-4-(R-phenyl)-1,3-thiazoles 4d,e

Appropriate 2-amino-4-aryl-thiazole **3d,e** (0.012 mol) was dissolved in 4 mL of phosphoric acid (80%). The solution was cooled with ice, and 1.8 mL of concentrated nitric acid was added dropwise during 5 min while keeping the temperature below 5°C. Then the solution of sodium nitrite (0.90 g; 0.013 mol) in 1.5 mL of water was added, and the solution of diazonium salt was left for 30 min. The solution of sodium azide (0.72 g; 0.02 mol) in 5 mL of water was added. Azide was extracted by diethyl ether (3 × 10 mL). Ether was evaporated in vacuo. Azides were used without the subsequent purification.

Synthesis of 1-(1,3-Thiazol-2-yl)-1*H*-1,2,3-triazole-4-carboxylic Acids 6a–j

Sodium (0.23 g, 0.01 mol) was added to 20 mL of absolute methanol. β-Ketoester **5** (0.01 mol) and the appropriate azide **4** (0.01 mol) was slowly added (cooling by ice water) to the obtained sodium methylate solution. The mixture was kept in an ice-water bath for 30 min and then slowly heated under reflux for 1 h. The solid sedimented. Hot water was added to dissolve the sediment (50 mL); if necessary, a solution of sodium hydroxide was added to increase pH to 11–12 and heated under reflux for 1 h. Hot solution was poured to a 10 mL of concentrated HCl and left to crystallize. The obtained solid was filtered, washed with water twice, and crystallized.

Data

5-Methyl-1-(1,3-thiazol-2-yl)-1*H*-1,2,3-triazole-4-carboxylic acid 6a. Yield: 42%; brown solid; mp 167–168°C (CH_2Cl_2). ^1H NMR: $\delta = 2.92$ (s, 3H, CH_3), 7.74 (d, 1 H, $^3J = 3.9$ Hz, H_{Tz}), 7.80 (d, 1 H, $^3J = 3.9$ Hz, H_{Tz}). MS (CI): $m/z = 211$ $[M^+ + 1]$. Anal. calcd. for $C_7H_6N_4O_2S$: C, 39.99; H, 2.88; N, 26.65. Found: C, 39.72; H, 2.94; N, 26.58.

5-Methyl-1-(4,5,6,7-tetrahydro-1,3-benzothiazol-2-yl)-1*H*-1,2,3-triazole-4-carboxylic acid 6b. Yield: 71%; white crystals; mp 154–155°C (EtOH–H_2O). ^1H NMR: $\delta = 1.85$–1.94 (m, 4H, CH_2), 2.72–2.76 (m, 2H, CH_2), 2.81–2.85 (m, 2H, CH_2), 2.86 (s, 3H, Me). MS (CI): $m/z = 265$ $[M^+ + 1]$. Anal. calcd. for $C_{11}H_{12}N_4O_2S$: C, 49.99; H, 4.58; N, 21.20. Found: C, 49.85; H, 4.73; N, 21.40.

1-(5-Carboxy-4-methyl-1,3-thiazol-2-yl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylic acid 6c. Yield: 64%; white crystals; mp 244–245°C (EtOH–H_2O). ^1H NMR: $\delta = 2.67$ (s, 3H, CH_3), 2.93 (s, 3H;, CH_3). MS (CI): $m/z = 269$ $[M^+ + 1]$. Anal. calcd. for $C_9H_8N_4O_4S$: C, 40.30; H, 3.01; N, 20.89. Found: C, 40.70; H, 3.21; N, 21.00.

5-Methyl-1-(4-phenyl-1,3-thiazol-2-yl)-1*H*-1,2,3-triazole-4-carboxylic acid 6d. Yield: 79%; white crystals; mp 175–176°C (EtOH–H_2O). ^1H NMR: $\delta = 3.02$ (s, 3H, CH_3), 7.33 (t, 1H, $J = 7.8$ Hz, 4-H_{Ph}), 7.44 (t, 2H, $J = 7.8$ Hz, 3,5-H_{Ph}), 7.95 (d, 2H, $J = 7.8$ Hz, 2,6-H_{Ph}), 8.06 (s, 1H, H_{Tz}). MS (CI): $m/z = 287$ $[M^+ + 1]$. Anal. calcd. for $C_{13}H_{10}N_4O_2S$: C, 54.53; H, 3.52; N, 19.57. Found: C, 54.25; H, 3.40; N, 19.70.

5-Methyl-1-[4-(4-methylphenyl)-1,3-thiazol-2-yl]-1*H*-1,2,3-triazole-4-carboxylic acid 6e. Yield: 82%; white crystals; mp 172–173°C (EtOH–H_2O). ^1H NMR: $\delta = 2.37$ (s, 3H, CH_3), 3.02 (s, 3H, CH_3), 7.23 (d, 2H, $J = 8.0$ Hz, 3,5-H_{Ar}), 7.82 (d, 2H, $J = 8.0$ Hz, 2,6-H_{Ar}), 7.99 (s, 1H, H_{Tz}). MS (CI): $m/z = 301$ $[M^+ + 1]$. Anal. calcd. for $C_{14}H_{12}N_4O_2S$: C, 55.99; H, 4.03; N, 18.65. Found: C, 56.11; H, 4.23; N, 18.61.

1-(5-Benzyl-1,3-thiazol-2-yl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylic acid 6f. Yield: 75%; white crystals; mp 157–158°C (EtOH–H_2O). ^1H NMR: $\delta = 2.88$ (s, 3H, CH_3), 4.24 (s, 2H, CH_2), 7.22–7.36 (m, 5H, H_{Ph}), 7.60 (s, 1H, H_{Tz}), 13.15 (br.s, 1H, COOH). MS (CI): $m/z = 301$ $[M^+ + 1]$. Anal. calcd. for $C_{14}H_{12}N_4O_2S$: C, 55.99; H, 4.03; N, 18.65. Found: C, 55.81; H, 3.79; N, 18.74.

5-Methyl-1-[5-(3-methylbenzyl)-1,3-thiazol-2-yl]-1*H*-1,2,3-triazole-4-carboxylic acid 6g. Yield: 71%; white crystals; mp 124–125°C (EtOH–H_2O). ^1H NMR: $\delta = 2.32$ (s, 3H, CH_3), 2.88 (s, 3H, CH_3), 4.18 (s, 2H, CH_2), 7.04 (d, 1H, $J = 7.2$ Hz, 4-H_{Ar}), 7.09 (d, 1H, $J = 7.2$ Hz, 6-H_{Ar}), 7.10 (s, 1H, 2-H_{Ar}), 7.20 (t, 1H, $J = 7.2$ Hz, 5-H_{Ar}), 7.60 (s, 1H, H_{Tz}), 13.16 (br.s, 1H, COOH). MS (CI): $m/z = 315$ $[M^+ + 1]$. Anal. calcd. for $C_{15}H_{14}N_4O_2S$: C, 57.31; H, 4.49; N, 17.82. Found: C, 57.52; H, 4.29; N, 17.94.

5-Methyl-1-[5-(4-methylbenzyl)-1,3-thiazol-2-yl]-1*H*-1,2,3-triazole-4-carboxylic acid 6h. Yield: 83%; white crystals; mp 158–159°C (EtOH–H_2O). ^1H NMR: $\delta = 2.32$ (s, 3H, CH_3), 2.89 (s, 3H, CH_3), 4.19 (s, 2H, CH_2), 7.12 (d, 2H,

$J = 8.0$ Hz, 3,5-H_{Ar}), 7.19 (d, 2H, $J = 8.0$ Hz, 2,6-H_{Ar}), 7.57 (s, 1H, H_{Tz}), 13.13 (br.s, 1H, COOH). MS (CI): $m/z = 315$ [$M^+ + 1$]. Anal. calcd. for $C_{15}H_{14}N_4O_2S$: C, 57.31; H, 4.49; N, 17.82. Found: C, 57.16; H, 4.38; N, 17.75.

1-[5-(4-Chlorobenzyl)-1,3-thiazol-2-yl]-5-methyl-1*H*-1,2,3-triazole-4-carboxylic 6i. Yield: 87%; white crystals; mp 183–184°C (EtOH–H_2O). ^{1}H NMR: $\delta = 2.80$ (s, 3H, CH_3), 4.23 (s, 2H, CH_2), 7.33 (s, 4H, H_{Ar}), 7.59 (s, 1H, H_{Tz}). MS (CI): $m/z = 335$ [$M^+ + 1$]. Anal. calcd. for $C_{14}H_{11}ClN_4O_2S$: C, 50.23; H, 3.31; N, 16.74. Found: C, 50.09; H, 3.26; N, 16.55.

1-(5-Benzyl-1,3-thiazol-2-yl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylic acid 6j. Yield: 79%; white crystals; mp 100–101°C (EtOH). ^{1}H NMR: $\delta = 4.18$ (s, 2H, CH_2), 7.20–7.34 (m, 5H, H_{Ph}), 7.39–7.47 (m, 6H, $H_{Ph} + H_{Tz}$). MS (CI): $m/z = 363$ [$M^+ + 1$]. Anal. calcd. for $C_{19}H_{14}N_4O_2S$: C, 62.97; H, 3.89; N, 15.46. Found: C, 62.78; H, 3.99; N, 15.54.

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