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Synthesis of Mesoionic 1,3,4-Thiadiazole-2-Thiolates

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Abstract: A reliable synthesis of C5-unsubstituted 1,3,4-thiadiazole-2-thiolates is described that avoids potentially explosive or laborious steps. This work presents a reliable method for preparing the starting material dithioformate from carbon disulfide and potassium or sodium tri-*sec*-butylhydroborates for the preparation of the mesoionic title compounds with potassium hydrazinecarbodithioates. New 1,3,4-thiadiazole-2-thiolates are presented, and missing structural analysis data of known derivatives are added (1D- and 2D-NMR, HR-ESI-MS, IR).

Keywords: mesoionic compound; potassium dithioformate; potassium methanedithioate; mesomeric betaine; hydrazines; selectride; sydnone; münchnone

1. Introduction

The first 1,3,4-thiadiazole-2-thiolate **1** was mentioned as early as 1895 by Busch et al. [1], making this compound one of the oldest representatives of mesoionic compounds [2]. These form a subgroup of the class of mesomeric betaines [3], which are characterized by an equal number of positive and negative charges delocalized within a common π-electron system of a heterocyclic ring system without any non-charged mesomeric structure. The oldest mesoionic compound mentioned in the literature is dehydrodithizone **2** (see Figure 1), which was described by Fischer and Besthorn as early as 1882 [4,5]. The most frequently cited representatives of mesoionic compounds in the literature, however, are derivatives from the sydnone and münchnone family, such as sydnones **3** [6–8], sydnonimines **4** [8,9], sydnone-methides **5** [10], münchnones **6** [11], or thioisomünchones **7** [12]. This is due to their synthetic potential as masked 1,3-dipoles [11,12], *N*-heterocyclic carbene precursors [9,10], or their biological activities [6,7].

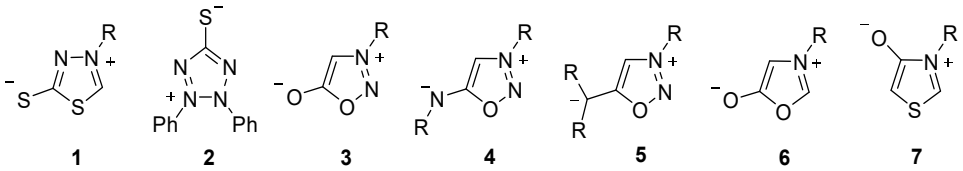


Figure 1. Examples of mesoionic compounds.

Among these examples, C5-unsubstituted 1,3,4-thiadiazole-2-thiolates in particular seem to be the least studied, perhaps because of their difficult synthetic accessibility to date. Nevertheless, this ring system was met with great interest. 1,3,4-Thiadiazole-2-thiolates were calculated in terms of their aromaticity [13] as well as their suitability as precursors for the formation of *N*-heterocyclic carbenes [14], and patented for several applications, e.g., in lithography [15]. Electronic absorption spectra [16], mass spectra [17], and electric

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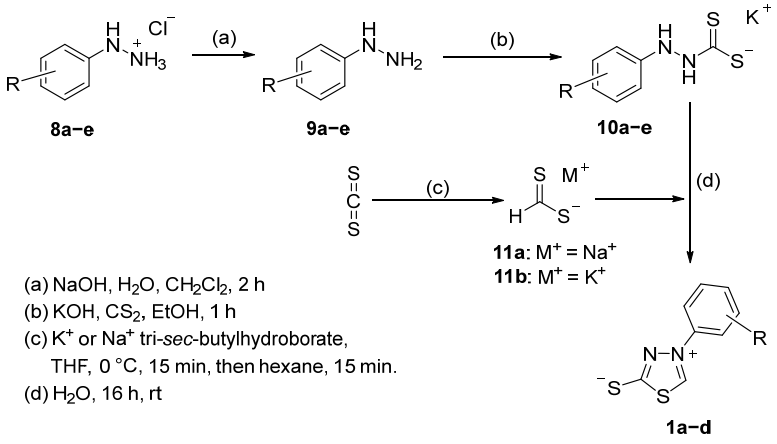
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dipole moments [18] were examined. So far, syntheses have almost exclusively led to 1,3,4-thiadiazole-2-thiolates that are substituted in the 5-position. For example, reactions of hydrazine-1-carbodithioates with acyl chlorides or aldehydes [19–21], syntheses starting from thiohydrazides and CS_2, or, less effectively, thiophosgene, and from hydrazides and carbon disulfide were described [22,23]. The often light- and moisture-sensitive dithioformates M^+ HCS_2^- are needed to synthesize C5-unsubstituted derivatives of 1,3,4-thiadiazol-2-thiolates. Dithioformates are available, for example, from chloroform in a methanolic solution of potassium sulfide under the exclusion of air [24]. According to the literature references, the dithioformates crystallize after concentrating the solution [25,26]. However, this reaction is warned against. It can cause explosions [27] and has been found to be unpredictable, as two out of three attempts lead to an eruption or explosion of the flask contents [28]. A modified version of the reaction was developed, but it requires very careful control of the reaction conditions to be safe [28]. Alternatively, a synthesis is described in which methanol is first reacted with elemental potassium and then treated with hydrogen sulfide, the excess of which must be removed with N_2 under reduced pressure. After the addition of more methanol and potassium, chloroform is added dropwise, which, after extensive work-up, yields potassium dithioformate [29]. Another synthesis reduces CS_2 with potassium tri-isopropylborohydride in THF [30]. Finally, it is mentioned in the literature that sodium dithioformate is obtained as a by-product when CS_2 reacts with $NaBH_4$ (or NaH) with carbon disulfide in the presence of tertiary amines during the preparation of amine-borane adducts [31]. The dithioformate, however, seemingly was not isolated. We report here a simple preparation of potassium and sodium dithioformate and use it in the synthesis of C5-unsubstituted 1,3,4-thiadiazole-2-thiolates. This method is effective and avoids handling elemental potassium or hydrogen sulfide.

2. Results and Discussion

The mesoionic 1,3,4-thiadiazole-2-thiolates, which were prepared in this work, were accessible via the reaction route shown in Scheme 1. Retrosynthetically, the heterocycles can be reduced to the corresponding *N*-arylated hydrazines **9a**–**d**, carbon disulfide, and the C1-building block dithioformate **11a**,**b** mentioned above (see Scheme 1).

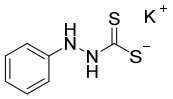
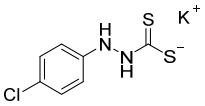
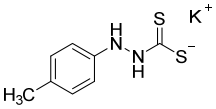
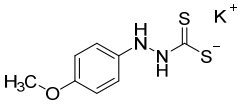
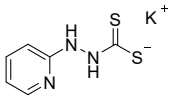


Scheme 1. Synthetic pathway of the title compounds.

The required hydrazines were obtained as hydrochlorides **8a**–**d** directly from the supplier and reacted with NaOH in aqueous solution to the corresponding free hydrazines **9a**–**e** [32] and, after extraction with DCM and drying over $MgSO_4$, were used for the subsequent reactions without further purification. Said hydrazines were dissolved in ethanolic potassium hydroxide solution and reacted with carbon disulfide [33]. The deprotonation

of hydrazines or amines in the presence of a strong base with subsequent addition of CS_2 is a synthetic approach for the formation of thioamides that is also used in modern literature [34]. The separate isolation of the free hydrazines was chosen since the direct treatment of the hydrochlorides with an excess of KOH and subsequent addition of CS_2 would result in inorganic side-products, such as KCl, which are unnecessarily hard to remove from the water-soluble potassium hydrazinecarbodithioates. During the addition of the disulfide, the corresponding potassium salts **10a**–**e** started to precipitate and the addition of diethyl ether (Et_2O) completed the precipitation. The resulting solids were filtered off and thoroughly washed with dichloromethane to remove any residual hydrazine, which usually results in analytically pure products. If necessary, the potassium salts **10a**–**e** can be recrystallized in methanolic solution and were isolated in good to very good yields (see Table 1).

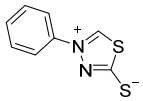
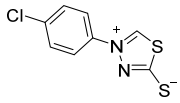
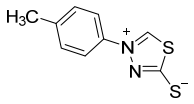
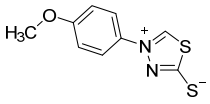
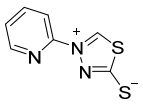
Table 1. Isolated potassium salts **10a**–**e**.

Compound Number	Compound Structure	Yield [%]
10a		91
10b		92
10c		84
10d		74
10e		66

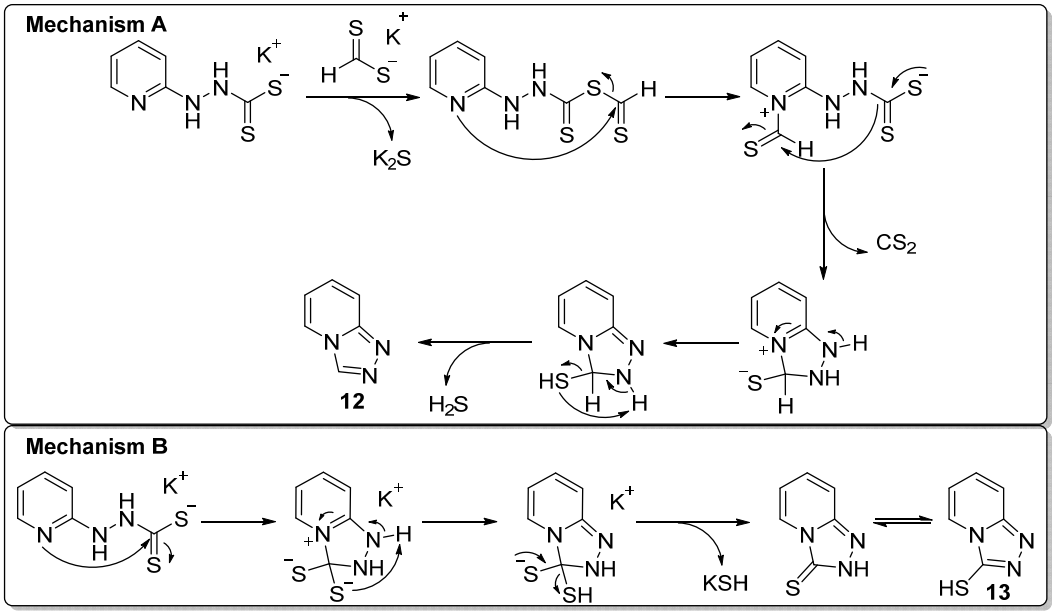
The second building block of the synthesis route is synthesized via the reduction of CS_2 with tri-*sec*-butylhydroborates (Selectrides, MERCK) in short reaction times and moderate yields. A 1 M solution of potassium or sodium tri-*sec*-butylhydroborates in *abs*. THF was added dropwise to a solution of CS_2 in *abs*. THF under ice cooling, which led to the formation of an intensely yellow solid. After dilution of the suspension with hexane, filtration, and extensive washing with hexane, the dithioformates **11a**,**b** were obtained as analytically pure solids. Described syntheses of the dithioformates by reduction of carbon disulfide with either $KB(OiPr)_3H$, $NaBH_4$, or NaH (*vide supra*) were not successful in our case. The mesoionic compounds **1a**–**e** were then smoothly obtained via the reaction of the corresponding potassium salts **10a**–**e** with the dithioformates **11a**,**b** in an aqueous medium. No significant difference in yield and reaction time was observed for the usage of either potassium or sodium dithioformate, and syntheses of the mesoionic compounds were conducted with the potassium dithioformate **11b** for the sake of uniform cations in the reaction. The mesoionic compounds precipitated from the aqueous solution, with the exception of **1e** (*vide infra*), and can thus be separated from their water-soluble starting materials after filtration and thorough washing with water. Hence, the described mesoionic heterocycles **1a**–**d** can be isolated in analytical purity without complex work-up. For rapid removal of residual water, the heterocycles were redissolved in MeOH, and the solvent was

removed under reduced pressure. This process was repeated three times, and the samples were dried to constant weight in a fine vacuum before gravimetric determination of the yield (see Table 2).

Table 2. Isolated mesoionic compounds **1a–e**.

Compound Number	Compound Structure	Yield [%]
1a		69
1b		60
1c		71
1d		65
1e		0

In contrast to the fast conversion of potassium salts **10a–d** for the syntheses of the heterocycles **1a–d**, no conversion to the anticipated mesoion **1e** was observed. Instead, a ring-closure reaction yielding [1,2,4]triazolo[4,3-*a*]pyridine **12** was observed following a competitive nucleophilic attack of the nitrogen of the pyridine ring at the dithioformate moiety, as described in the proposed mechanism in Scheme 2 (mechanism **A**). This stands in analogy to literature procedures for the syntheses of **12** via, e.g., base-promoted oxidative iodination of the corresponding hydrazone [35] or the addition of C1-building blocks such as formic acid to the corresponding hydrazine [36]. However, to the best of our knowledge, this is the first reported case of the isolation of **12** starting from thioformates. In addition to the formation of the bicyclic system **12**, conversion of the potassium salt **10e** to [1,2,4]triazolo[4,3-*a*]pyridine-3-thiol **13** was achieved by stirring **10e** in an aqueous solution at 100 °C for 48 h without the addition of dithioformates **11a**,**b** (Scheme 2, mechanism **B**), in analogy to the direct addition of carbon disulfide to 2-hydrazinepyridine **9e** in aqueous solution as described in the literature [37].



Scheme 2. Proposed mechanisms for the formation of **12** and **13**.

3. Materials and Methods

3.1. General Experimental Information

Commercially available materials were used without further purification unless noted otherwise. Solvents were dried according to established procedures and stored under nitrogen. The reaction progress was monitored by thin-layer chromatography (TLC) on silica-coated aluminum sheets from Merck (Darmstadt, Germany; 60 F_{254}). NMR spectra were measured on the FT-NMR Devices Avance Neo (400 MHz) and Avance III (600 MHz) from Bruker (Ettlingen, Germany) and analyzed with TopSpin 3.5 from Bruker. Chemical shifts (δ) are given in ppm relative to the residual solvent d_6-DMSO (^{1}H (d_6-DMSO): δ = 2.50 ppm, ^{13}C (d_6-DMSO): δ = 39.52 ppm) [38]. Coupling constants J are given in hertz (Hz), with the following abbreviations for multiplicity: s (singlet), d (doublet), dd (doublet of doublet), ddd (doublet of doublet of doublet), dt (doublet of triplet), t (triplet), and td (triplet of doublet). Signals without analyzable coupling are marked as m (multiplet). The prefix app. (apparent) is used to highlight that the observed multiplicity is a result of vague subordinated coupling. For the ^{13}C/DEPT-spectra, (+) is added for carbons bonded to one or three hydrogens and (−) for carbons bonded to two hydrogens. Quaternary carbon atoms are denoted with the symbol (o). The hydrazines were directly purchased from the supplier (Merck, TCI) as free base or as the hydrochloride and, if necessary, converted to the free hydrazine according to literature procedures ([32], general procedure 1, *vide infra*) and were used without further purification.

3.2. Experimental Procedures and Characterization of Compounds

(1) General procedure for the conversion of hydrazine hydrochlorides to free hydrazines

To a solution of the corresponding hydrochloride (1 equiv.) in H_2O (10 mL/mmol), NaOH (2 equiv./equiv. of HCl) and DCM (8 mL/mmol) were added, and the solution was vigorously stirred at rt for 2 h. The organic layer was separated, and the aqueous solution was extracted with DCM (3×). The combined organic layers were washed once with water, dried over $MgSO_4$, and the solvent was removed under reduced pressure after filtration. The obtained free hydrazines were generally not suitable for long-term storage and were used directly without further purification.

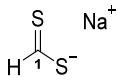
(2) General procedure for the synthesis of potassium hydrazinecarbodithioates:

The corresponding free hydrazine (1 equiv.) was added to a solution of KOH (1 equiv.) in *abs*. EtOH, followed by the dropwise addition of carbon disulfide (2 equiv.) over the course of 15 min at rt (the product may already precipitate during the addition). After complete addition, the solution was stirred for 1 h and diluted with Et_2O. The precipitate was collected by filtration, washed with DCM, and recrystallized if necessary. All salts isolated in this work are highly hygroscopic.

(3) General procedure for the synthesis of 1,3,4-thiadiazolium-2-thiolates:

A solution of the corresponding potassium hydrazinecarbodithioate (1 equiv.) in water (5 mL/mmol) was treated with potassium dithioformate and stirred at rt for 16 h. The precipitated mesoionic compound was collected by filtration, thoroughly washed with water, and dried under vacuum. For optimized yields, the use of freshly prepared potassium hydrazinecarbodithioates and dithioformates is advised.

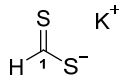
3.2.1. Sodium Dithioformate (Sodium Methanedithioate) (**11a**)



Sodium tri-*sec*-butylhydroborate (1 M solution in *abs*. THF, 10.000 g, 11.20 mL, 48.51 mmol) was added dropwise over the course of 15 min. at 0 °C with a N_2-purged syringe to a stirred solution of carbon disulfide (7.386 g, 5.83 mL, 97.01 mmol) in *abs*. THF (10 mL). After complete addition, *n*-hexane (50 mL) was added and stirring was continued for an additional 15 min. The precipitated salt was isolated by filtration, thoroughly washed with *n*-hexane, and dried under vacuum to obtain **11a** (2.219 g, 22.16 mmol, **45%**) as a yellow solid.

^{1}H-NMR (600 MHz, d_6-DMSO): δ = 12.03 (s, 1H, H-1) ppm. **^{13}C-NMR** (150 MHz, d_6-DMSO): δ = 245.8 (+, 1C, C-1) ppm. **M.P.**: 74–76 °C; **IR** (ATR) v = 3181, 2886, 2103, 1634, 1428, 1189, 1139, 1123, 1049, 998, 884, 767, 739, 682, 498, 473 cm^{-1}; **HR-ESI-MS**: calcd. for $[C_2H_2S_4Na]^-$ (dimeric sodium salt): 176.8943; found: 176.8938.

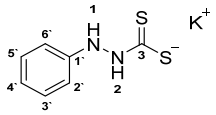
3.2.2. Potassium Dithioformate (Potassium Methanedithioate) (**11b**)



Potassium tri-*sec*-butylhydroborate (1 M solution in *abs*. THF, 10.000 g, 10.95 mL, 45.00 mmol) was added dropwise over the course of 15 min at 0 °C with a N_2-purged syringe to a stirred solution of carbon disulfide (6.851 g, 5.41 mL, 89.99 mmol) in *abs*. THF (10 mL). After complete addition, *n*-hexane (50 mL) was added, and stirring was continued for an additional 15 min. The precipitated salt was isolated by filtration, thoroughly washed with *n*-hexane, and dried under vacuum to obtain **11b** (2.162 g, 18.60 mmol, **41%**) as a yellow solid.

^{1}H-NMR (600 MHz, d_6-DMSO): δ = 12.04 (s, 1H, H-1) ppm. **^{13}C-NMR** (150 MHz, d_6-DMSO): δ = 245.8 (+, 1C, C-1) ppm. **M.P.**: 69–71 °C; **IR** (ATR) v = 3277, 2102, 1626, 1590, 1377, 1349, 1262, 1193, 1114, 1039, 993, 884, 833, 768, 733, 667, 581, 529 cm^{-1}; **HR-ESI-MS**: calcd. for $[C_2H_2S_4K]^-$ (dimeric potassium salt): 192.8682; found: 192.8676.

3.2.3. Potassium Phenylhydrazinecarbodithioate (**10a**)

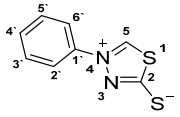


According to general procedure (2), phenylhydrazine (1.000 g, 0.91 mL, 9.25 mmol) was added to a solution of KOH (0.512 g, 9.25 mmol) in *abs*. EtOH (25 mL), followed by the addition of carbon disulfide (1.408 g, 1.12 mL, 18.50 mmol). Full precipitation was achieved by the addition of Et_2O (50 mL). Compound **10a** (1.882 g, 8.46 mmol, **91%**) was isolated as a colorless solid. If necessary, recrystallization of **10a** was achieved from MeOH.

^{1}H-NMR (600 MHz, d_6-DMSO): δ = 10.01 (d, J = 5.2 Hz, 1H, H-2), 7.80 (d, J = 5.2 Hz, 1H, H-1), 7.12 (app. ddd, J = 11.6; 6.1; 4.2 Hz, 2H, H-3′, H-5′), 6.75 (app. dd, J = 8.5; 1.0 Hz, 2H, H-2′, H-6′), 6.71–6.76 (m, 1H, H-4′) ppm. **^{13}C-NMR** (150 MHz, d_6-DMSO): δ = 212.6 (o, 1C, C-3), 149.6 (o, 1C, C-1′), 128.4 (+, 2C, C-3′, C-5′), 119.1 (+, 1C, C-4′), 114.1 (+, 2C, C-2′, C-6′) ppm. **M.P.**: 136–138 °C (decomposition); **IR** (ATR) v = 3372, 3031, 2062, 1596, 1492, 1452, 1407, 1329, 1303, 1232, 1205, 1176, 1122, 1069, 1027, 992, 893, 833, 754, 692, 668, 647, 580, 534, 493 cm^{-1}; **HR-ESI-MS**: calcd. for $[C_7H_7N_2S_2]^-$: 183.0056; found: 183.0054.

The analytical data obtained complement the literature [39].

3.2.4. 4-Phenyl-1,3,4-Thiadiazolium-2-Thiolate (**1a**)

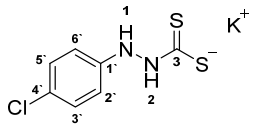


According to general procedure (3), potassium dithioformate (**11b**, 0.262 g, 2.25 mmol) was added to a solution of potassium phenylhydrazinecarbodithioate (**10a**, 0.250 g, 1.13 mmol) in water (6 mL). Compound **1a** (0.152 g, 0.78 mmol, **69%**) was isolated as a light-yellow solid.

^{1}H-NMR (600 MHz, d_6-DMSO): δ = 10.39 (s, $^1J_{C,H}$ = 215.3 Hz, 1H, H-5), 7.92–7.91 (m, 2H, H-3′, H-5′), 7.64–7.63 (m, 3H, H-2′, H-4′, H-6′) ppm. **^{13}C-NMR** (150 MHz, d_6-DMSO): δ = 185.1 (o, 1C, C-2), 153.5 (+, 1C, C-5), 138.1 (o, 1C, C-1′), 130.8 (+, 1C, C-4′), 129.8 (+, 2C, C-2′, C-6′), 122.1 (+, 2C, C-3′, C-5′) ppm. **M.P.**: 193–195 °C; **IR** (ATR) v = 2979, 2903, 1589, 1491, 1449, 1336, 1310, 1261, 1153, 1100, 1046, 1003, 914, 847, 812, 752, 685, 659, 627, 551, 523, 466 cm^{-1}; **HR-ESI-MS**: calcd. for $[C_8H_6N_2S_2+Na]^+$: 216.9865; found: 216.9864.

The analytical data obtained complement the literature [1].

3.2.5. Potassium 1-(4′-Chlorophenyl)Hydrazinecarbodithioate (**10b**)

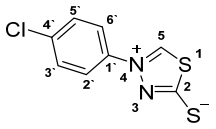


According to general procedure (2), (4-chlorophenyl)hydrazine (1.000 g, 7.01 mmol) was added to a solution of KOH (0.394 g, 7.01 mmol) in *abs*. EtOH (25 mL), followed by the addition of carbon disulfide (1.068 g, 0.85 mL, 14.03 mmol). Full precipitation was achieved by the addition of Et_2O (50 mL). Compound **10b** (1.672 g, 6.51 mmol, **92%**) was isolated as a colorless solid. If necessary, recrystallization of **10b** was achieved from MeOH.

^{1}H-NMR (600 MHz, d_6-DMSO): δ = 9.96 (app. s, 1H, H-2), 7.77 (app. s(br), 1H, H-1), 7.15 (d, J = 8.7 Hz, 2H, H-3′, H-5′), 6.73 (d, J = 8.7 Hz, 2H, H-2′, H-3′) ppm. **^{13}C-NMR** (150 MHz, d_6-DMSO): δ = 213.7 (o, 1C, C-3), 148.7 (o, 1C, C-1′), 128.1 (+, 2C, C-3′, C-5′), 122.1 (+, 1C, C-4′), 115.3 (+, 2C, C-2′, C-6′) ppm. **M.P.**: 122–124 °C (decomposition); **IR** (ATR)

v = 3355, 3236, 3176, 2062, 1634, 1594, 1486, 1444, 1313, 1273, 1231, 1207, 1184, 1131, 1087, 1048, 992, 821, 733, 664, 606, 540, 501, 485 cm^{-1}; **HR-ESI-MS**: calcd. for $[C_7H_6ClN_2S_2]^-$: 216.9666; found: 216.9663.

3.2.6. 4-(4′-Chlorophenyl)-1,3,4-Thiadiazolium-2-Thiolate (**1b**)

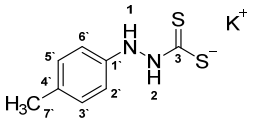


According to general procedure (3), potassium dithioformate (**11b**, 0.226 g, 1.95 mmol) was added to a solution of potassium 1-(4′-chlorophenyl)hydrazinecarbodithioate (**10b**, 0.250 g, 0.97 mmol) in water (5 mL). Compound **1b** (0.135 g, 0.59 mmol, **60%**) was isolated as a light-yellow solid.

^{1}H-NMR (600 MHz, d_6-DMSO): δ = 10.41 (s, $^1J_{C,H}$ = 214.9 Hz, 1H, H-5), 7.95 (d, J = 8.6 Hz, 2H, H-2′, H-6′), 7.72 (d, J = 8.6 Hz, 2H, H-3′, H-5′) ppm. **^{13}C-NMR** (150 MHz, d_6-DMSO): δ = 185.1 (o, 1C, C-2), 154.1 (+, 1C, C-5), 136.8 (o, 1C, C-1′), 135.2 (o, 1C, C-4′), 129.8 (+, 2C, C-3′, C-5′), 124.0 (+, 2C, C-2′, C-6′) ppm. **M.P.**: 201–203 °C; **IR** (ATR) v = 3436, 3052, 3000, 2938, 2902, 1589, 1493, 1409, 1331, 1230, 1091, 1044, 1009, 851, 820, 720, 640, 608, 580, 52, 496, 471, 416 cm^{-1}; **HR-ESI-MS**: calcd. for $[C_8H_5ClN_2S_2+Na]^+$: 250.9475; found: 250.9474.

The analytical data obtained complement the literature [40].

3.2.7. Potassium 1-(P-Tolyl)Hydrazinecarbodithioate (**10c**)

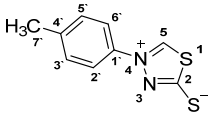


According to general procedure (2), *p*-tolylhydrazine (1.000 g, 8.19 mmol) was added to a solution of KOH (0.459 g, 8.19 mmol) in *abs*. EtOH (25 mL), followed by the addition of carbon disulfide (1.246 g, 0.99 mL, 16.37 mmol). Full precipitation was achieved by the addition of Et_2O (50 mL). Compound **10c** (1.631 g, 6.90 mmol, **84%**) was isolated as a colorless solid. If necessary, recrystallization of **10c** was achieved from MeOH.

^{1}H-NMR (600 MHz, d_6-DMSO): δ = 9.97 (d, J = 3.6 Hz, 1H, H-2), 7.71 (d, J = 3.9 Hz, 1H, H-1), 6.93 (d, J = 7.9 Hz, 2H, H-3′, H-5′), 6.66 (d, J = 8.0 Hz, 2H, H-2′, H-6′), 2.18 (s, 3H, H-7′) ppm. **^{13}C-NMR** (150 MHz, d_6-DMSO): δ = 212.1 (o, 1C, C-3), 147.2 (o, 1C, C-1′), 128.8 (+, 2C, C-3′, C-5′), 127.7 (o, 1C, C-4′), 114.4 (+, 2C, C-2′, C-6′), 20.2 (+, 1C, C-7′) ppm. **M.P.**: 179–181 °C (decomposition); **IR** (ATR) v = 3367, 3030, 2918, 2861, 2062, 1609, 1508, 1446, 1395, 1380, 1328, 1301, 1245, 1210, 1151, 1111, 1031, 993, 814, 775, 665, 501 cm^{-1}; **HR-ESI-MS**: calcd. for $[C_8H_9N_2S_2]^-$: 197.0213; found: 197.0206.

The analytical data obtained complement the literature [41].

3.2.8. 4-(P-Tolyl)-1,3,4-Thiadiazolium-2-Thiolate (**1c**)

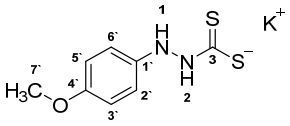


According to general procedure (3), potassium dithioformate (**11b**, 0.212 g, 2.12 mmol) was added to a solution of potassium 1-(*p*-tolyl)hydrazinecarbodithioate (**10c**, 0.250 g, 1.06 mmol) in water (5 mL). Compound **1c** (0.157 g, 0.75 mmol, **71%**) was isolated as a light-yellow solid.

^{1}H-NMR (600 MHz, d_6-DMSO): δ = 10.33 (s, $^1J_{C,H}$ = 214.8 Hz, 1H, H-5), 7.79 (d, J = 8.6 Hz, 2H, H-2′, H-6′), 7.43 (d, J = 8.3 Hz, 2H, H-3′, H-5′), 2.40 (s, 3H, H-7′) ppm. **^{13}C-NMR** (150 MHz, d_6-DMSO): δ = 185.1 (o, 1C, C-2), 152.7 (+, 1C, C-5), 140.8 (o, 1C, C-4′), 135.9 (o, 1C, C-1′), 130.2 (+, 2C, C-3′, C-5′), 121.8 (+, 2C, C-2′, C-6′), 20.7 (+, 1C, C-7′) ppm. **M.P.**: 191–193 °C; **IR** (ATR) v = 2985, 2925, 1602, 1504, 1476, 1453, 1334, 1311, 1291, 1257, 1231, 1179, 1164, 1098, 1045, 1020, 1008, 939, 857, 802, 782, 638, 614, 528, 475 cm^{-1}; **HR-ESI-MS**: calcd. for $[C_9H_8N_2S_2+Na]^+$: 231.0021; found: 231.0022.

The analytical data obtained complement the literature [40].

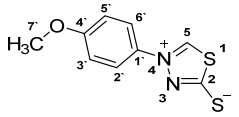
3.2.9. Potassium 1-(4′-Methoxyphenyl)Hydrazinecarbodithioate (**10d**)



According to general procedure (2), (4-methoxyphenyl)hydrazine (1.000 g, 7.24 mmol) was added to a solution of KOH (0.406 g, 7.24 mmol) in *abs*. EtOH (25 mL), followed by the addition of carbon disulfide (1.102 g, 0.87 mL, 14.48 mmol). Full precipitation was achieved by the addition of Et_2O (50 mL). Compound **10d** (1.358 g, 5.38 mmol, **74%**) was isolated as a colorless solid. If necessary, recrystallization of **10d** was achieved from MeOH.

^{1}H-NMR (600 MHz, d_6-DMSO): δ = 10.02 (app. s, 1H, H-2), 7.66 (app. s(br), 1H, H-1), 6.75 (d, J = 9.1 Hz, 2H, H-3′, H-5′), 6.72 (d, J = 9.1 Hz, 2H, H-2′, H-6′), 3.66 (s, 3H, H-7′) ppm. **^{13}C-NMR** (150 MHz, d_6-DMSO): δ = 211.7 (o, 1C, C-3), 153.2 (o, 1C, C-4′), 143.3 (o, 1C, C-1′), 115.8 (+, 2C, C-2′, C-6′), 113.9 (+, 2C, C-3′, C-5′), 55.3 (+, 1C, C-7′) ppm. **M.P.**: 164–166 °C (decomposition); **IR** (ATR) v = 3376, 3283, 3164, 3000, 2957, 2933, 2834, 2061, 1597, 1543, 1504, 1455, 1439, 1297, 1241, 1170, 1136, 1110, 1021, 874, 825, 725, 625, 577, 511 cm^{-1}; **HR-ESI-MS**: calcd. for $[C_8H_9N_2OS_2]^-$: 213.0162; found: 213.0158.

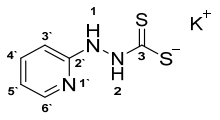
3.2.10. 4-(4′-Methoxyphenyl)-1,3,4-Thiadiazolium-2-Thiolate (**1d**)



According to general procedure (3), potassium dithioformate (**11b**, 0.230 g, 1.98 mmol) was added to a solution of potassium 1-(4′-methoxyphenyl)hydrazinecarbodithioate (**10d**, 0.250 g, 0.99 mmol) in water (5 mL). Compound **1d** (0.146 g, 0.65 mmol, **65%**) was isolated as a light-yellow solid.

^{1}H-NMR (600 MHz, d_6-DMSO): δ = 10.26 (s, $^1J_{C,H}$ = 214.7 Hz, 1H, H-5), 7.85 (d, J = 8.8 Hz, 2H, H-2′, H-6′), 7.15 (d, J = 8.8 Hz, 2H, H-3′, H-5′), 3.84 (s, H, H-7′) ppm. **^{13}C-NMR** (150 MHz, d_6-DMSO): δ = 185.0 (o, 1C, C-2), 160.7 (o, 1C, C-4′), 151.8 (+, 1C, C-5), 131.4 (o, 1C, C-1′), 123.6 (+, 2C, C-2′, C-6′), 114.7 (+, 2C, C-3′, C-5′), 55.8 (+, 1C, C-7′) ppm. **M.P.**: 202–204 °C; **IR** (ATR) v = 3061, 2968, 2929, 2889, 2837, 2037, 1610, 1593, 1512, 1464, 1450, 1439, 1358, 1346, 1312, 1266, 1182, 1123, 1047, 1025, 1008, 857, 826, 785, 650, 587, 510 cm^{-1}; **HR-ESI-MS**: calcd. for $[C_9H_8N_2OS_2+Na]^+$: 246.9970; found: 246.9970.

3.2.11. Potassium 1-(Pyridine-2-Yl)Hydrazinecarbodithioate (**10e**)

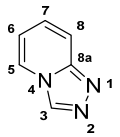


According to general procedure (2), 2-hydrazinopyridine (1.000 g, 9.16 mmol) was added to a solution of KOH (0.514 g, 9.16 mmol) in *abs*. EtOH (25 mL), followed by the

addition of carbon disulfide (1.395 g, 1.11 mL, 18.33 mmol). Full precipitation was achieved by the addition of Et_2O (50 mL). Compound **10e** (1.361 g, 6.09 mmol, **66%**) was isolated as a yellow solid after recrystallization from ethyl acetate.

^{1}H-NMR (600 MHz, d_6-DMSO): δ = 9.95 (d, J = 2.6 Hz 1H, H-2), 8.10 (app. s, 1H, H-1), 8.04 (app. dd, J = 4.9; 1.0 Hz, 1H, H-6′), 7.51 (app. td, J = 7.7; 1.8 Hz, 1H, H-4′), 6.69 (app. dt, J = 5.7; 1.3 Hz, 1H, H-3′), 6.61 (app. d, J = 8.4 Hz, 1H, H-5′) ppm. **^{13}C-NMR** (150 MHz, d_6-DMSO): δ = 213.5 (o, 1C, C-3), 160.4 (o, 1C, C-2′), 147.4 (+, 1C, C-6′), 137.2 (+, 1C, C-4′), 114.7 (+, 1C, C-3′), 107.5 (+, 1C, C-5′) ppm. **M.P.**: 119–121 °C (decomposition); **IR** (ATR) v = 3537, 3402, 3235, 3139, 2966, 2911, 2898, 1632, 1597, 1573. 1501, 1476, 1443, 1430, 1390, 1325, 1300, 1267, 1147, 1091, 1050, 993, 852, 772, 696, 653. 623, 571, 558, 535, 474 cm^{-1}; **HR-ESI-MS**: calcd. for $[C_6H_6N_4S_2]^-$: 184.0009; found: 184.0007.

3.2.12. [1,2,4]Triazolo[4,3-a]Pyridine (**12**)

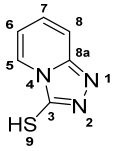


Potassium dithioformate (**11b**, 0.260 g, 2.24 mmol) was added to a solution of potassium 2-(pyridine-2-yl)hydrazinecarbodithioate (**10e**, 0.250 g, 1.12 mmol) in water (5 mL) and stirred at 100 °C for 48 h. After cooling to room temperature, the aqueous solution was extracted with DCM (3 × 10 mL) and the combined organic layers were washed with water (1 × 15 mL). After drying the organic solution with $MgSO_4$ and removal of the solvent, **12** (0.042 g, 0.35 mmol, **31%**) was isolated as yellow, viscous oil.

^{1}H-NMR (600 MHz, d_6-DMSO): δ = 9.26 (s, 1H, H-3), 8.57 (dt, J = 6.9, 1.1 Hz, 1H, H-5), 7.76 (app. dd, J = 9.3, 1.0 Hz, 1H, H-8), 7.35 (ddd, J = 9.3, 6.6, 1.1 Hz, 1H, H-7), 6.96 (td, J = 6.8, 0.8 Hz, 1H, H-6) ppm. **^{13}C-NMR** (150 MHz, d_6-DMSO): δ = 148.5 (o, 1C, C-8a), 136.5 (+, 1C, C-3), 128.0 (+, 1C, C-7), 125.1 (+, 1C, C-5), 115.0 (+, 1C, C-8), 113.6 (+, 1C, C-6) ppm.

The analytical data obtained are in accordance with the literature [35].

3.2.13. [1,2,4]Triazolo[4,3-a]Pyridine-3-Thiol (**13**)



A solution of potassium 2-(pyridine-2-yl)hydrazinecarbodithioate (**10e**, 0.100 g, 0.45 mmol) in water (5 mL) was stirred at 100 °C for 48 h. After cooling to room temperature, the aqueous solution was extracted with DCM (3 × 10 mL) and the combined organic layers are washed with water (1 × 15 mL). After drying the organic solution with $MgSO_4$ and removal of the solvent, **13** (0.031 g, 0.12 mmol, **46%**) was isolated as a yellow solid.

^{1}H-NMR (400 MHz, d_6-DMSO): δ = 14.67 (s(br), 1H, H-9), 8.26 (dt, J = 7.1, 1.2 Hz, 1H, H-5), 7.61 (dt, J = 9.4, 1.1 Hz, 1H, H-8), 7.46 (ddd, J = 9.5, 6.5, 1.2 Hz, 1H, H-7), 6.99 (td, J = 7.1, 1.0 Hz, 1H, H-6) ppm. **^{13}C-NMR** (100 MHz, d_6-DMSO): δ = 159.1 (o, 1C, C-3), 146.2 (o, 1C, C-8a), 131.0 (+, 1C, C-7), 125.0 (+, 1C, C-5), 115.5 (+, 1C, C-8), 113.9 (+, 1C, C-6) ppm.

The analytical data obtained are in accordance with the literature [42].

Supplementary Materials: NMR, IR, and high-resolution MS spectra of all compounds.

Author Contributions: Conceptualization, S.R.K. and A.S.; methodology, S.R.K.; validation, S.R.K. and A.S.; formal analysis, A.S.; investigation, S.R.K.; resources, S.R.K. and A.S.; data curation, S.R.K.;

writing—original draft preparation, S.R.K.; writing—review and editing, A.S.; visualization, A.S.; supervision, A.S.; project administration, A.S.; funding acquisition, A.S. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Materials. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

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