



1,2,5-Thiadiazole 2-oxides: selective synthesis, structural characterization, and electrochemical properties



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ABSTRACT

A new general procedure for the selective synthesis of 1,2,5-thiadiazole 2-oxides (including fused derivatives) **8a,b,c,g,h** from the reaction of *vic*-glyoximes with S₂Cl₂ and pyridine in acetonitrile was elaborated together with general procedure for the synthesis of 1,2,5-thiadiazoles **7a–i**, **10**, **12**, and **14** from the same starting materials and reagents. Molecular structures of 3,4-dimethyl-1,2,5-thiadiazole 2-oxide **8a** and [1,2,5]thiadiazolo[3,4-*b*]quinoxaline **10** were confirmed by single-crystal X-ray diffraction. Electrochemical properties of 1,2,5-thiadiazole 2-oxides **8** were studied by cyclic voltammetry and different behavior was observed for monocyclic and benzo-fused derivatives. With compounds **8g** and **17**, previously unknown deoxygenation of 2,1,3-benzothiadiazole 1-oxides was discovered by electrochemical reduction, and resulted 2,1,3-benzothiadiazoles **7g** and **19** were detected in the forms of their radical anions by EPR spectroscopy combined with DFT calculations.

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1. Introduction

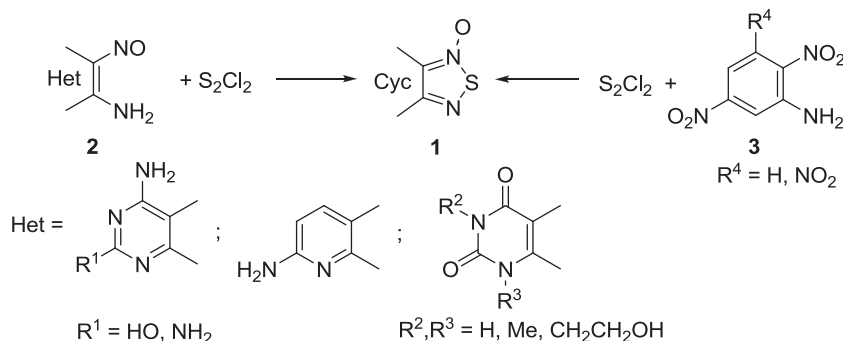
1,2,5-Thiadiazoles and their benzo-fused derivatives (i.e., 2,1,3-benzothiadiazoles) have been known for many years, and their synthesis, chemical and physical properties were extensively studied and reviewed.^{1–4} Apart their use in numerous branches of chemistry, medicine,^{1,2} and agriculture,^{5–8} they were found to be an efficient electron acceptors and were employed as building blocks of many actual or potential molecule-based functional materials for organic electronics⁹ and spintronics (in this case as ligands for coordination compounds of paramagnetic metal cations).¹⁰ Recently, they were used in the synthesis of thermally stable radical-anion (RA) salts,¹¹ revealing antiferromagnetic exchange interactions in their spin systems,¹² and conductive charge-transfer complexes also possessing photoconductivity.¹³

Based on DFT calculations of electron affinity, it was expected that *N*-oxides of the aforementioned compounds, i.e., 1,2,5-thiadiazole 2-oxides and 2,1,3-benzothiadiazole 1-oxides, can also be good precursors of stable RAs isolable in the form of salts.¹⁴

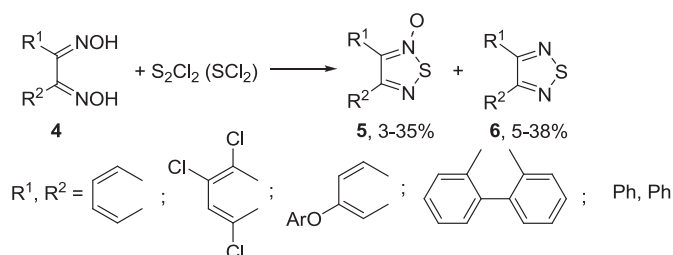
It should be emphasized that in contrast to well-studied chemistry of *S*-oxides and *S,S*-dioxides of 1,2,5-thiadiazoles including electrochemistry and potential applications in materials science (see Ref. 15 and references therein), the chemistry of *N*-oxides of this ring system is still in its infancy. 1,2,5-Thiadiazole 2-oxides and their derivatives are rare compounds. According to search in the SciFinder and Reaxys databases, only 16 compounds were described. Benzo- and heterocyclic fused derivatives have been obtained in the reaction of sulfur monochloride with *o*-aminonitroso^{16–18} and *o*-aminonitro¹⁹ precursors (Scheme 1).

Unfortunately in both cases starting materials are limited especially in the case of non-fused derivatives. *vic*-Dioximes **4** are more available precursors for the synthesis of 1,2,5-thiadiazole 2-oxides. Their reactions with sulfur monochloride (S₂Cl₂) or sulfur dichloride (SCl₂) led to mixtures of thiadiazole oxides **5** and non-oxygenated 1,2,5-thiadiazoles **6** both in low yield (Scheme 2).^{20,21}

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Scheme 1. Synthesis of 1,2,5-thiadiazole 2-oxides (**1**) from *o*-aminonitroso (**2**) and *o*-aminonitro (**3**) derivatives.



Scheme 2. Synthesis of 1,2,5-thiadiazole 2-oxides (**5**) from *vic*-dioximes (**4**).

Moreover, to date, conclusive proof of structure for non-fused 1,2,5-thiadiazole 2-oxides has not been provided, nor have studies appeared on their physical and chemical properties. In this paper we report a study of a reaction between *vic*-dioximes and sulfur monochloride, a selective synthesis of 1,2,5-thiadiazole 2-oxides and corresponding 1,2,5-thiadiazoles covering monocyclic and fused derivatives, their structural characterization and electrochemical properties.

2. Results and discussion

2.1. Synthesis and structure elucidation

In an effort to improve the synthesis of 1,2,5-thiadiazole 2-oxides, we re-investigated the reaction of commercial dimethylglyoxime with sulfur monochloride—a versatile reagent in organic chemistry.^{22,23} Treatment of dimethylglyoxime with S_2Cl_2 in dimethylformamide (DMF)—a solvent, which is frequently used in S_2Cl_2 reactions^{22,23}—at low ($-25\text{ }^\circ\text{C}$) to room temperature gave 3,4-dimethyl-1,2,5-thiadiazole **7a** in moderate yields. The type of base used was important for the success of reactions with S_2Cl_2 in other solvents (chloroform or acetonitrile). Reaction of dimethylglyoxime with a two-fold excess of S_2Cl_2 and 1,4-diazabicyclooctane (DABCO) in chloroform at $-5\text{ }^\circ\text{C}$ led to the desired 3,4-dimethyl-1,2,5-thiadiazole 2-oxide **8a** although in low yield (35%) together with unreacted dimethylglyoxime. Our attempts to increase the yield of *N*-oxide **8a** by using an excess of S_2Cl_2 and DABCO led to conversion of **8a** to thiadiazole **7a** even at low temperature ($-25\text{ }^\circ\text{C}$). Our best results for the synthesis of *N*-oxide **8a** were achieved by treating dimethylglyoxime with two-fold excess of S_2Cl_2 and pyridine in acetonitrile at $5\text{ }^\circ\text{C}$ for 1 h, which gave 3,4-dimethyl-1,2,5-thiadiazole 2-oxide **8a** selectively in a moderate 53% yield (Scheme 3).

Further on, we extended this reaction to other *vic*-glyoximes. Monocyclic (methyl, phenyl, and morphol-4-yl substituted) and benzo- and cyclohexano-fused 1,2,5-thiadiazole 2-oxides **8a–c,g,h** were obtained in moderate yields. *N*-Oxides **8d,e** containing

electron-withdrawing substituents ($R=\text{CN}, \text{Cl}$) were found to be unstable and readily deoxygenated to the corresponding thiadiazoles **7d** and **7e**, respectively, whereas in the case of bis(dimethylamino)glyoxime and (9*E*,10*E*)-phenanthrene-9,10-dione dioxime thiadiazole oxides **8f,i** were not isolated from the reaction mixtures. IR spectroscopy showed the presence of characteristic stretching medium frequencies of *N*-oxide group for all 1,2,5-thiadiazole 2-oxides **8** at $1352\text{--}1364\text{ cm}^{-1}$; the mass spectra indicated major loss of an oxygen with moderate intensity presumably for conversion to 1,2,5-thiadiazoles.

Synthesized 1,2,5-thiadiazole 2-oxides **8a–c,g,h** were converted into the thiadiazoles **7** in high yields by treatment with S_2Cl_2 and pyridine in acetonitrile at room temperature.

Interesting and partly unexpected results were obtained when diaminoglyoximes were involved in the reaction with sulfur monochloride. Treatment of (2*Z*,3*Z*)-1,4-dihydroquinoxaline-2,3-dione dioxime **9** with S_2Cl_2 in the presence of pyridine in acetonitrile under similar conditions led to the formation of [1,2,5]thiadiazolo[3,4-*b*]quinoxaline **10** in moderate yield (Scheme 4). In that case two processes take place simultaneously—the formation of thiadiazole ring from dioxime moiety and dehydration of dihydropiperazine into aromatic pyrazine ring presumably by action of sulfur monochloride. The structure of compound **10** (Fig. 1) was confirmed by single-crystal X-ray diffraction (XRD). As compared with the 2,1,3-benzothiadiazole **7g**,²⁴ the structure of thiadiazoloquinoxaline **10** revealed very similar geometry within the thiadiazole ring. In the crystal, shortened intermolecular contacts $S2\cdots N9$ of 3.085 \AA (normal contact $S\cdots N$ is 3.45 \AA)²⁵ lead to formation of infinite chains of molecules along *b* axis. Additionally, weak $\pi\cdots\pi$ interaction of neighboring chains is observed featuring interplanar separation of $3.32\text{--}3.36\text{ \AA}$.

Under similar conditions, (5*Z*,6*Z*)-[1,2,5]oxadiazolo[3,4-*b*]pyrazine-5,6(4*H*,7*H*)-dione dioxime **11** gave tricyclic bis([1,2,5]thiadiazolo)-[3,4-*b*;3',4'-*e*]pyrazine **12**²⁷ in moderate yield (Scheme 5). In that case three reactions occurred: formation of thiadiazole ring from dioxime, exchange of an oxygen atom in a 1,2,5-oxadiazole ring by a sulfur atom, and aromatization of piperazine ring. The yields of aromatic thiadiazoles **10** and **12** can be improved substantially (73% and 66%, correspondingly) by treatment of fused glyoximes **9** and **11** with S_2Cl_2 in DMF presumably owing the better solubility of glyoximes in this solvent.

Reaction of an easily available²⁸ diaminoglyoxime **13** with S_2Cl_2 in the presence of pyridine in acetonitrile gave [1,2,5]thiadiazolo[3,4-*c*] [1,2,5]thiadiazole **14** in moderate yield (Scheme 6). Thiadiazolothiadiazole **14** is one of the most useful precursor for the preparation of persistent RA.^{3,11,14} The described method is the most simple and convenient for the synthesis of this compound and opens new possibilities for its use in the construction of new materials.

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