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The Acid and/or Thermal Mediated Ring Contraction of 4*H*-1,2,6-Thiadiazines To Afford 1,2,5-Thiadiazoles

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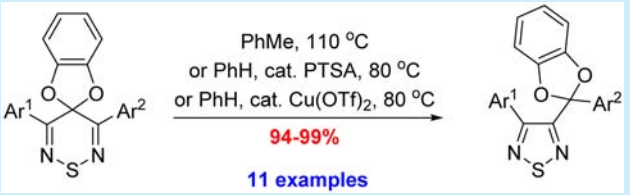
Supporting Information

ABSTRACT: A near-quantitative acid and/or thermal mediated ring contraction of 3′,5′-diarylspiro(benzo[*d*][1,3]dioxole-2,4′-[1,2,6]thiadiazines) affords 3-aryl-4-(2-arylbenzo[*d*][1,3]dioxol-2-yl)-1,2,5-thiadiazoles. The reaction scope was studied providing 11 examples of this ring contraction. A double Wagner−Meerwein reaction mechanism is proposed.



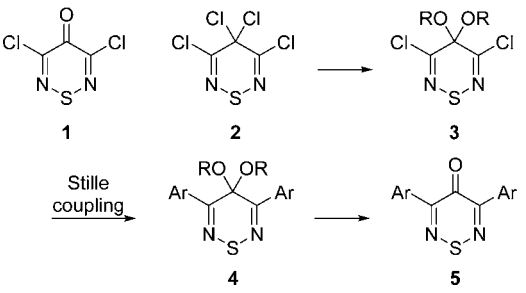
1,2,5-Thiadiazoles (Figure 1) have been known for over 100 years.[1] Important commercial drugs that contain non S-oxidized 1,2,5-thiadiazoles include Timolol (β-blocker) and Tizanidine (antispasmolytic).[1b] Areno-fused 1,2,5-thiadiazoles also find uses as electron acceptor components in organic electronic devices.[2]

Figure 1. Structures of 1,2,5-thiadiazole and 4*H*-1,2,6-thiadiazine with IUPAC numbering in red and common bonds highlighted in blue.

Not surprisingly, extensive efforts have been made to develop new syntheses of 1,2,5-thiadiazoles.[1] Commonly used synthetic strategies involve the introduction of sulfur to N−C−C−N scaffolds,[3] while others invoke the use of hazardous reagents such as trithiazyl trichloride[4] or tetrasulfur tetranitride[5] to introduce in one step both sulfur and nitrogen atoms to available C−C and C−C−N scaffolds.[1] Less common are syntheses that invoke ring transformations of other heterocycles,[1,6] and to the best of our knowledge, the only example of a ring contraction that leads to a 1,2,5-thiadiazole is the thermally mediated loss of sulfur from 1,4,2,6-dithiadiazine.[7]

For several years now, we have worked on the closely related non-S-oxidized 4*H*-1,2,6-thiadiazine (Figure 1), which shares five of the same ring atoms with the same connectivity as 1,2,5-thiadiazole. Non-S-oxidized 4*H*-1,2,6-thiadiazines have been known for over 40 years, and their chemistry has mainly focused on the available 3,5-dichloro-4*H*-1,2,6-thiadiazin-4-one (**1**)[8a] and 3,4,4,5-tetrachloro-4*H*-1,2,6-thiadiazine (**2**)[8b] scaffolds (Scheme 1). To date, this chemistry has been limited to halogen displacement,[8a,9] oxidation of sulfur,[9c] and condensations on the C-4 position.[10]

Scheme 1. Structure of 3,5-Dichloro-4*H*-1,2,6-thiadiazin-4-one (1) and Selected Reactions of 3,4,4,5-Tetrachloro-4*H*-1,2,6-thiadiazine (2)



Despite the structural similaries between these two hetarenes, and to the best of our knowledge, no ring contractions of 1,2,6-thiadiazines into 1,2,5-thiadiazoles have been reported.

Recently, we demonstrated the 4,4-ketalization of 3,4,4,5-tetrachloro-4*H*-1,2,6-thiadiazine (**2**) to afford 4,4-(dialkyl/diaryl)oxy-3,5-dichloro-4*H*-1,2,6-thiadiazines **3** that can be bisarylated via Stille coupling chemistry to give the 3,5-diaryl analogues **4** and deprotected to afford the 3,5-diaryl-4*H*-1,2,6-thiadiazin-4-ones **5** (Scheme 1).[11]

Interestingly, in the case of the phenylation of the catechol ketalized thiadiazine **3a** (R = 1,2-C_6H_4) the Stille reactions had to be performed at 80 °C because at ca. 90 °C the reactions became complex.[11b] Analysis of the product mixture from the reaction run at 90 °C revealed an unexpected product **6a**, isolated as colorless needles, mp 103−104 °C (from *t*-BuOMe/-40 °C) [see Supporting Information (SI) Table S1, entries 1 and 2].

Mass spectrometry (*m*/*z* 358) and elemental analysis gave a molecular formula of $C_{21}H_{14}N_2O_2S$ indicating **6a** was isomeric to the expected 3′,5′-diphenylspiro(benzo[*d*][1,3]dioxole-2,4′-[1,2,6]thiadiazine) (**4a**). ^{1}H and ^{13}C NMR spectroscopy of

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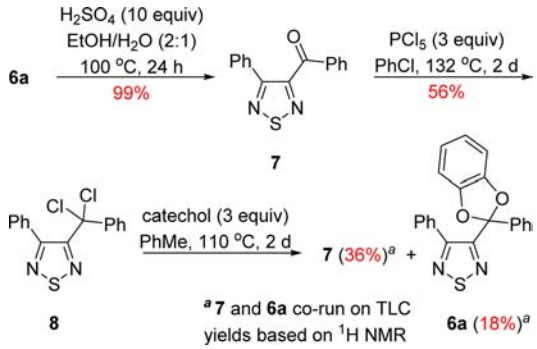
compound **6a** (see SI, Section S5), however, suggested a less symmetrical molecule that contained a catechol unit and two dissimilar phenyl groups. Hydrolysis with concd H_2SO_4 gave the known 3-benzoyl-4-phenyl-1,2,5-thiadiazole (**7**),[12] which reacted with PCl_5 to give the geminal dichloride **8**. Subsequent treatment of dichloride **8** with catechol gave an inseparable mixture of the starting compound **6a** and the 1,2,5-thiadiazole **7** (Scheme 2).

Scheme 2. Selected Reactions of the Unknown 6a



Finally, X-ray crystallography supported the structure of the unknown product to be 3-phenyl-4-(2-phenylbenzo[*d*][1,3]-dioxol-2-yl)-1,2,5-thiadiazole (**6a**) (Figure 2).

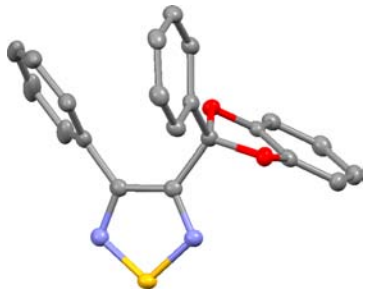


Figure 2. X-ray structure of 3-phenyl-4-(2-phenylbenzo[*d*][1,3]dioxol-2-yl)-1,2,5-thiadiazole (**6a**) (CCDC 1483490). Thermal ellipsoids are at 50% probability. Hydrogens ommited for clarity.

Interestingly, the known routes to 3-benzoyl-4-phenyl-1,2,5-thiadiazole (**7**) used hazardous tetrasulfur tetranitride[12,13] [***Caution***: Explosive] or difficult to prepare trithiazyl trichloride[14] and resulted in low to moderate yields (20−60%).[12−14]

The formation of the 1,2,5-thiadiazole **6a** was puzzling, but further studies were revealing: when the Stille reaction of tributylphenyltin with 3′,5′-dichlorospiro(benzo[*d*][1,3]-dioxole-2,4′-[1,2,6]thiadiazine) (**3a**) was carried out at higher temperatures (ca. 110 °C) the thiadiazole **6a** was observed as the only product in 92% yield. This suggested that the originally anticipated product, the 3,5-diphenylthiadiazine catechol ketal **4a**, was an intermediate to the observed thiadiazole **6a**. Differential scanning calorimetry (DSC) performed on the ketal **4a** revealed a sharp melting point (onset: 35.7 °C peak max: 46.2 °C) followed by a broad decomposition (onset: 114.7 °C, peak max: 140.5 °C) (see SI, Section S3). Analysis of the DSC pan contents after the decomposition point identified only the presence of the 1,2,5-thiadiazole **6a**, supporting that its formation was a result of a thermal rearrangement of the 1,2,6-thiadiazine **4a**. The thermal reaction was also performed on a larger scale (0.1 mmol) at ca. 150 °C for 10 min under an argon atmosphere and afforded the 1,2,5-thiadiazole **6a** in 66% yield. By introducing a solvent (e.g., PhH, MeCN, dioxane, PhMe, or PhCl) the reaction temperatures can be lowered, and while this led to longer reaction times, the product was obtained in near-quantitative yields (see SI, Table S2).

Moreover, this ring contraction was catalyzed by both Lewis (Zn^{2+}, Cu^{2+}, Cu^{+} and Mg^{2+} salts) and Brønsted acids (PTSA, $MeSO_3H$, TFA, AcOH, and picric acid), enabling reactions to be carried out in PhH at ca. 80 °C (see SI, Table S2). Note that when neat concd H_2SO_4 was used only the deprotected ketone **5a** (Ar = Ph, 74%) was observed.[11b] Three optimized reactions conditions were identified: Condition A: thermal (PhMe at 110 °C, 3.5 h, 94%); Condition B: Brønsted acid catalyzed [dry PTSA (10 mol %) in PhH at 80 °C, 2 d, 98%]; and Condition C: Lewis acid catalyzed [$Cu(OTf)_2$ (2 mol %) in PhH at 80 °C, 2 d, 98%] (see SI, Table S2).

To investigate this unexpected rearrangement further, several control experiments were performed. These included heating the 1,2,6-thiadiazine **4a** in the presence of 1 equiv of various spin traps [*e.g.*, 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), 1,4-benzoquinone, 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT) and tocopherol], but no change in the reaction times or product yields was noted suggesting the absence of radical intermediates. Furthermore, the ring contraction of the 1,2,6-thiadiazine **4a** to the 1,2,5-thiadiazole **6a** was irreversible: subsequent thermal or acid treatment (TFA, 100 °C) of the thiadiazole gave only recovered thiadiazole **6a**. This was not surprising since 1,2,5-thiadiazole is aromatic (I_A = 104, cf. benzene I_A = 100)[15] and the starting 1,2,6-thiadiazine is a nonaromatic heterocycle. Finally, attempts to transform 3,5-diphenyl-4*H*-1,2,6-thiadiazin-4-one (**5a**) into 3-benzoyl-4-phenyl-1,2,5-thiadiazole (**7**) using thermolysis (xylene at *ca.* 139 °C), neat, or in the presence of acids (PTSA, TFA, $AlCl_3$) or bases (Hünigs, *t*-BuOK) failed and gave only degradation of the starting thiadiazinone.

We then prepared a series of 3,5-diaryl-1,2,6-thiadiazine ketals **4a−t** (see SI) to investigate their ability to rearrange into 1,2,5-thiadiazoles **6** under the optimum reaction conditions (A−C) identified above. In general, the ring contraction worked well with the catechol protected ketals bearing 3,5-(het)aryl substituents, but the presence of 3,5-dialkynyl, 3,5-dimethoxy, or 3,5-diphenoxy substituents led mainly to degradation. Furthermore, the reaction failed for the ethylene glycol protected ketals, even under forcing conditions (see SI).

Nevertheless, interesting electronic effects were noted for the 3,5-(het)aryl-substituted catechol protected ketals: aryl groups bearing electron-releasing groups such as 4-Me, 4-MeO, and 4-BnO (Table 1, entries 2−4) led to shorter reaction times, while electron-withdrawing groups such as 4-F and 4-O_2N (Table 1, entries 5 and 6) led to slower reactions. In the case of the 4-O_2N substituted analogue (Table 1, entry 7), high reaction temperatures (ca. 190 °C) were needed to consume all the starting material. Somewhat surprisingly, the hetaryl-substituted analogues **4j** (Ar^1/Ar^2 = fur-2-yl) and **4k** (Ar^1/Ar^2 = thien-2-yl) reacted considerably slower than the 3,5-diphenyl-substituted 1,2,6-thiadiazine (Table 1, entries 11 and 12); the reasons for this are unclear.

The reactions of unsymmetrical diarylthiadiazines **4g**, **4h** and **4i** were also informative. The thermal and acid catalyzed ring contraction of 3-phenyl-5-(4-methoxyphenyl)-1,2,6-thiadiazine **4g** gave a mixture of two inseparable 1,2,5-thiadiazoles (**6g**/**6h**,

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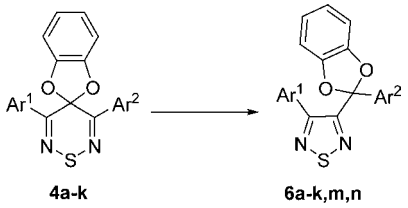
Table 1. Conversion of 1,2,6-Thiadiazines 4 (0.1 mmol) into 1,2,5-Thiadiazoles 6 under Thermolysis (Cond. A: PhMe at 110 °C) (See SI Table S3 for Cond. B and C)



entry	Ar^1	Ar^2	time (h)	yield **6** (%)
1	Ph		3	**6a** (94)
2	4-Tol		1	**6b** (98)
3	4-$MeOC_6H_4$		0.5	**6c** (99)
4	4-$BnOC_6H_4$		1	**6d** (98)
5	4-FC_6H_4		4.5	**6e** (98)
6	4-$O_2NC_6H_4$		24	**6f** (9)[a]
7	4-$O_2NC_6H_4$		0.3	**6f** (86)[b]
8	Ph	4-$MeOC_6H_4$	1	**6g/6h** (98)[c]
9	4-$O_2NC_6H_4$	Ph	3.5	**6i/6j** (98)[d]
10	4-$O_2NC_6H_4$	4-$MeOC_6H_4$	1	**6k** (95)
11	fur-2-yl		24	**6m** (84)
12	thien-2-yl		6	**6n** (99)

[a]Recovered starting material 88%. [b]Reaction run in biphenyl at *ca.* 190 °C. [c]Inseparable mixture of **6g** and **6h** (**6g/6h**, 82:18). [d]Inseparable mixture of **6i** and **6j** (**6i/6j**, 83:17).

~4.6:1 by ^{1}H NMR) with the electron-rich 4-$MeOC_6H_4$ group migrating preferentially in the major product **6g**. Similarly, the ring contraction of the 3-(4-nitrophenyl)-5-phenyl-1,2,6-thiadiazine **4h** also gave a mixture of two inseparable 1,2,5-thiadiazoles (**6i/6j**, ~4.9:1 by ^{1}H NMR) with the electron-rich phenyl group migrating preferentially in the major product **6i**. In both cases the ratio of the 1,2,5-thiadiazole isomers was not dramatically affected by the nature of the reaction conditions (i.e., Cond. A, B, or C; see SI Table S4). Furthermore, the thermal and acid catalyzed ring contraction of the 3-(4-methoxyphenyl)-5-(4-nitrophenyl)-1,2,6-thiadiazine (**4i**) was 100% regioselective giving only a single product **6k** (94–96%) where the migrating group was the 4-$MeOC_6H_4$; the structure of thiadiazole **6k** was supported by X-ray analysis (Figure 3).

A tentative mechanism for this ring contraction can be proposed based on the above-mentioned experimental evidence: first, the thermal reaction is promoted by either mild Brønsted or Lewis acids, and second, for the 3,5-diaryl-substituted 1,2,6-thiadiazines there was preferential migration

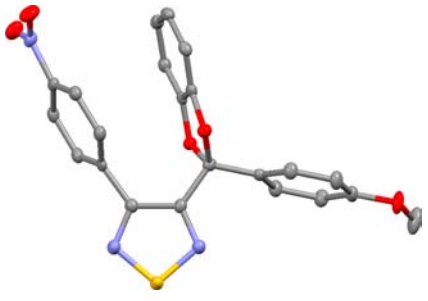
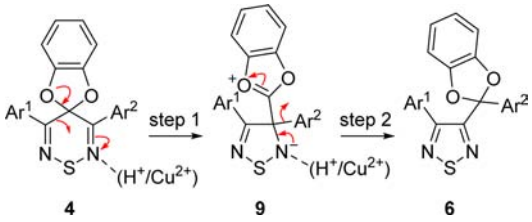


Figure 3. X-ray structure of 3-(4-methoxyphenyl)-5-(4-nitrophenyl)-1,2,6-thiadiazine (**6k**) (CCDC-1483491). Thermal ellipsoids are at 50% probability. Hydrogens ommited for clarity.

of the more electron rich aryl group. The above suggests two consecutive Wagner–Meerwein shifts: the first [1,2]-shift leads to the ring contracted 1,2,5-thiadiazole and can be assisted by both electron release from the ketal oxygens and electron pull from the thiadiazine sp^2 nitrogen atom (Scheme 3, step 1).

Scheme 3. Proposed Mechanism for the Thermal and Acid-catalyzed Ring Contraction of 1,2,6-Thiadiazine 4 into 1,2,5-Thiadiazole 6



Since step 1 formally requires a buildup of negative charge at either the thiadiazine C3 or C5 atoms, then the carbon bearing the more electron-stabilizing group is more likely to migrate (i.e., the one with the more electron-withdrawing substituents). Step 1 can also be promoted by acid catalysis via protonation or coordination of the thiadiazine sp^2 nitrogen atom, which not only stabilizes the formation of the negative charge on nitrogen but also potentially activates the same nitrogen by forming an iminium species prior to the ring contraction. The second [1,2]-shift leads to the migration of the aryl group to the C2 position of the benzodioxole of **9** and is similarly promoted by a *push–pull* effect: electron release from the neighboring 1,2,5-thiadiazole sp^3 nitrogen and electron withdrawal from the now positively charged benzo[1,3]dioxolium group (Scheme 3, step 2). Clearly, there should be preferential protonation of the thiadiazine nitrogen that is conjugated to the more electron-rich arene which then activates that arene to migrate to the oxonium.

Satisfactory explanations for the failure of the ethylene glycol protected ketals to undergo the ring contraction and also the unexpected sluggishness of the fur-2-yl and thien-2-yl analogues remain to be resolved, but tentatively we propose that since these [1,2]-shifts are promoted by *push–pull* effects of neighboring heteroatoms, it may be that orbital alignments of their lone pairs and the bonds being formed or broken play important roles that need deeper analysis; X-ray analysis of the 3,5-bis(4-nitrophenyl)-1,2,6-thiadiazine **4f** (see SI, Section S4) reveals a shallow boat conformation for the thiadiazine core and a nonsymmetrical geometry for the aryl and catechol substituents.

While there are many well-known ring contractions mediated by Favorskii,[16] pinacol,[17] Wolff,[18] and benzilic acid rearrangements,[19] none of these appears to fit this present example, which is more analogous to an α-ketol[20] or α-hydroxy imine[21] rearrangement.

In conclusion, 3,5-diaryl-1,2,6-thiadiazine 4,4-catechol ketals **4** can be thermally ring contracted to afford 1,2,5-thiadiazoles **6**. The reaction can be catalyzed by both mild Lewis and Brønsted acids. Tentatively, the ring contraction proceeds via a double Wagner–Meerwein rearrangement, where the first migration favors the more electron-poor aryl group. Further work is required to better understand the reaction mechanism and scope.

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■ ASSOCIATED CONTENT

Supporting Information

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Reaction optimization discussion, Experimental Section, X-ray data for **4f**, **6a**, and **6k**, and NMR spectra for all new compounds (PDF)
Crystallographic data for **4f** (CIF)
Crystallographic data for **6a** (CIF)
Crystallographic data for **6k** (CIF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to the memory of Prof. Charles W. Rees (1927−2006).

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