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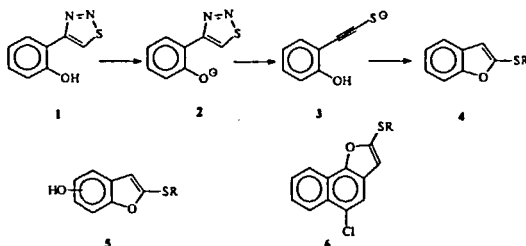
## New Ring Cleavage Reactions and Recyclizations Starting from 1,2,3-Thiadiazoles

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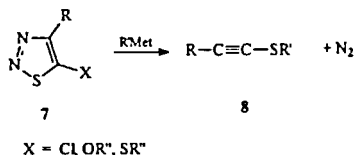
**Keywords:** 1,2,3-thiadiazoles; alkynes; ring cleavage; cyclization; benzofurans

4-Monosubstituted 1,2,3-thiadiazoles are known to decompose in the presence of base to afford the alkynethiolates. When a suitable nucleophilic function is present, a cyclization can occur. Starting from 4-(*o*-hydroxyphenyl)-1,2,3-thiadiazole **1**, benzofurans **4** were obtained after reaction with an alkylating agent.<sup>[1]</sup> In an <sup>1</sup>H-NMR spectroscopic study, we observed that both the phenolate **2** and the alkynethiolate **3** are intermediates in this reaction. Dihydroxyphenyl or hydroxynaphthyl substituted 1,2,3-thiadiazole derivatives were also converted to the corresponding hydroxybenzofuran and naphthothiophene systems **5** and **6**, respectively.

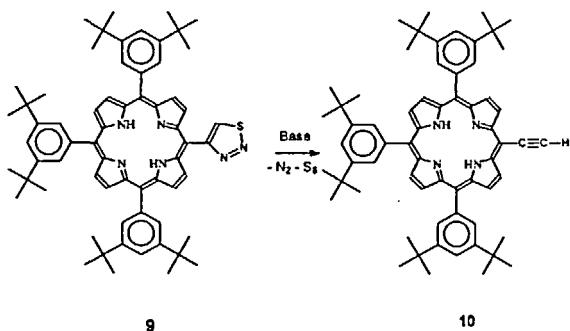


Disubstituted 1,2,3-thiadiazoles **7** ( $R = Cl$ ) are attacked by organometallic ( $Met = Li, MgBr$ ) reagents at the sulfur atom with loss of nitrogen. When a leaving group is present, the result is an alkyne sulfide **8**. Alkoxide, phenoxide or thiophenoxide bases substitute at the carbon and leave the 1,2,3-thiadiazole system of **7** ( $R = OR', SR'$ ) intact. The latter products afford the same alkyne sulfides **8** when treated with *n*-butyllithium. The alternative loss of butylsulfanyl anion does not occur. This seems to

indicate that the ring cleavage process occurs concertedly with the leaving of the 5-substituent.<sup>[2]</sup>



When connected to a porphyrin moiety, 4-monosubstituted 1,2,3-thiadiazoles 9 will not give the expected alkynethiolate on reaction with base, but instead lose sulfur and nitrogen simultaneously to afford the alkynes 10. The acidity of the thiadiazole H-5 is lowered significantly by conjugation to the porphyrin, which is in the dianion form, allowing this alternative process. This unexpected result constitutes a new method for the generation of interesting *meso*-ethynyl substituted porphyrins.<sup>[3]</sup>



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### References

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- [2] M. Voets, M. Smet and W. Dehaen, submitted.
- [3] S. Smeets and W. Dehaen, manuscript in preparation.