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## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

### THE SYNTHESIS OF 2,5-DIHYDROXYBENZO-1,3,2-DITHIAZOLYLUM AND 2,7-DICARBONYL NAPHTHA-1,3,2-DITHIAZOLYLUM CATIONS

Aaron Mailman<sup>a</sup>; Jack Passmore<sup>a</sup>

<sup>a</sup> University of New Brunswick, Fredericton, New Brunswick, Canada

Online publication date: 12 August 2010

**To cite this Article** Mailman, Aaron and Passmore, Jack(2004) 'THE SYNTHESIS OF 2,5-DIHYDROXYBENZO-1,3,2-DITHIAZOLYLUM AND 2,7-DICARBONYL NAPHTHA-1,3,2-DITHIAZOLYLUM CATIONS', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 4, 977 — 978

**To link to this Article:** DOI: 10.1080/10426500490429527

**URL:** <http://dx.doi.org/10.1080/10426500490429527>

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## THE SYNTHESIS OF 2,5-DIHYDROXYBENZO-1,3,2-DITHIAZOLYLIUM AND 2,7-DICARBONYL NAPHTHA-1,3,2-DITHIAZOLYLIUM CATIONS

Aaron Mailman and Jack Passmore  
University of New Brunswick, Fredericton,  
New Brunswick, Canada

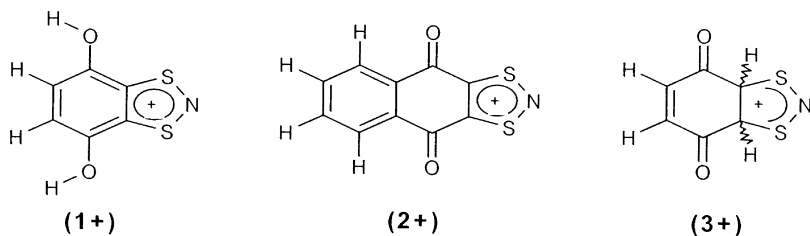
(Received August 17, 2003; accepted October 3, 2003)

*Keywords:* Cycloaddition; dithionitronium cation

The cycloaddition chemistry of the dithionitronium cation ( $\text{SNS}^+$ ) has led to the synthesis of dithiadiazolyl ( $\text{CNSNS}^+$ ,  $\text{CNSSN}^+$ ) and dithiazolyl ( $\text{CSNSC}^+$ ) ring systems from the corresponding nitriles and alkynes respectively.<sup>1</sup> Olefins are isolobal with both alkynes and nitriles and can undergo cycloaddition with one or two stoichiometric aliquots of olefin because of the two mutually perpendicular  $\pi$ -manifolds of  $\text{SNS}^+$ . The chemistry of  $\text{SNS}^+$  with extended  $\pi$ -systems has not yet been investigated beyond the case of benzene, where an electrophilic substitution results in the sulfur protonated substitution product, likely  $\text{C}_6\text{H}_5\text{SNSH}^+$ .<sup>4</sup> Wolmershauer first described the synthesis of benzo-fused 1,3,2-dithiazolylium chloride salt on a preparative scale,<sup>2</sup> which was characterized by x-ray crystallography.<sup>3</sup>

Preliminary investigations of the extended  $\pi$ -systems of 1,4-benzoquinone and 1,4-naphthoquinone with  $\text{SNS}^+$  have been shown by x-ray crystallography to be 2,5-dihydroxybenzo-1,3,2-dithiazolylium (**1**<sup>+</sup>  $\text{AsF}_6^-$ ) and 2,7-dicarbonylnaphtha-1,3,2-dithiazolylium (**2**<sup>+</sup>  $\text{AsF}_6^-$ ) salts (Figure 1). The salt (**1**) has been characterized by multinuclear NMR [ $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ,  $^{19}\text{F}$ , HMQC, COSY], infrared spectroscopy, and supported by DFT calculations (B3LYP/6-311++G\*\*). The intermediate (**3**) was found to be thermodynamically unfavorable in the gas phase and suggests that it will not be observed in solution or solid state. Both salts (**1**) and (**2**) show a similar layered motif, forming columns in the solid state, and few contacts between the anion and the  $\text{C}_2\text{S}_2\text{N}^+$  ring are observed in the case of (**1**).

Address correspondence to Jack Passmore, Department of Chemistry, University of New Brunswick, Fredericton, NB E3B 5A3, Canada. E-mail: passmore@unb.ca



**FIGURE 1** Dithiazolylium salts.

The simplicity of these reactions allows easy access to new derivatives of benzo-fused 1,3,2-dithiazolylium cations and subsequent reduction may yield potentially new, useful synthetic materials with interesting magnetic properties.

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