

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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>

Sulfur Transfer in A Three-Component System Including Phenyl Azide, Aromatic Thione and Sterically Crowded Tetramethylcyclobutanethione

Grzegorz Mloston^a; Heinz Heimgartner^b

^a Department of Org. & Appl. Chemistry, University of Lodz, Poland ^b Institute of Organic Chemistry, University of Zurich, Switzerland

To cite this Article Mloston, Grzegorz and Heimgartner, Heinz(1994) 'Sulfur Transfer in A Three-Component System Including Phenyl Azide, Aromatic Thione and Sterically Crowded Tetramethylcyclobutanethione', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 95: 1, 355 — 357

To link to this Article: DOI: 10.1080/10426509408034236

URL: <http://dx.doi.org/10.1080/10426509408034236>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SULFUR TRANSFER IN A THREE-COMPONENT SYSTEM INCLUDING PHENYL AZIDE, AROMATIC THIONE AND STERICALLY CROWDED TETRAMETHYLCYCLOBUTANETHIONE

Grzegorz MLOSTON*

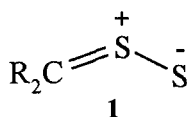
Department of Org. & Appl. Chemistry, University of Lodz, Poland

Heinz HEIMGARTNER

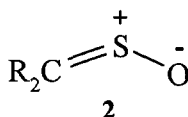
Institute of Organic Chemistry, University of Zurich, Switzerland

Abstract A new access to thiosulfines generated in a reaction system containing thiocarbonyl compounds and phenyl azide is described.

Thiocarbonyl-S-sulfides (thiosulfines) **1** belong to the class of sulfur centered 1,3-dipoles, they are considered as sulfur analogues of the much better known thiocarbonyl-S-oxides (sulfines) **2**.

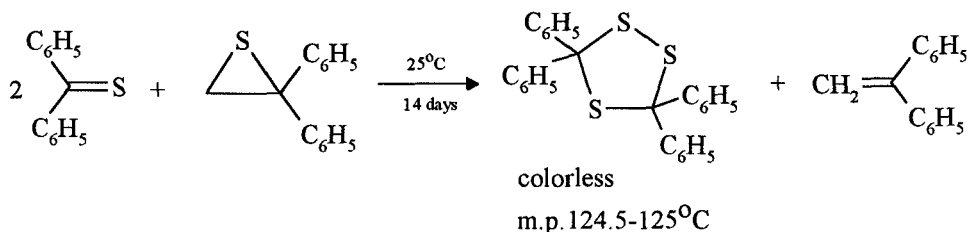


Thiocarbonyl-S-sulfides
(Thiosulfines)

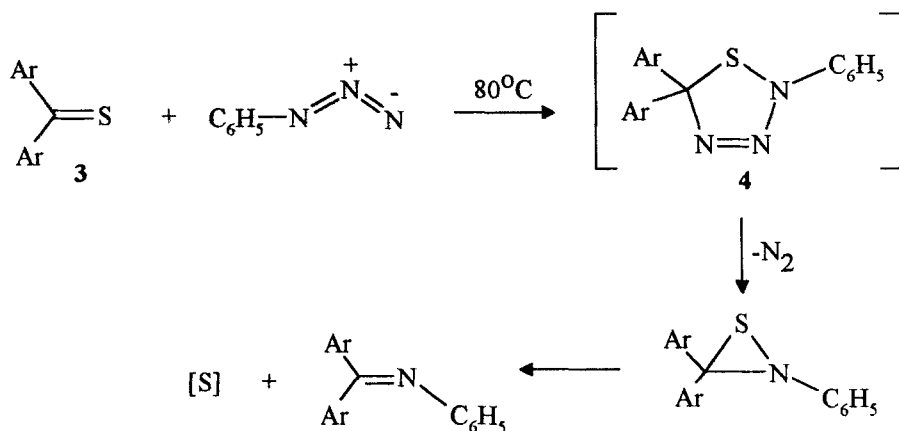


Thiocarbonyl-S-oxides
(Sulfines)

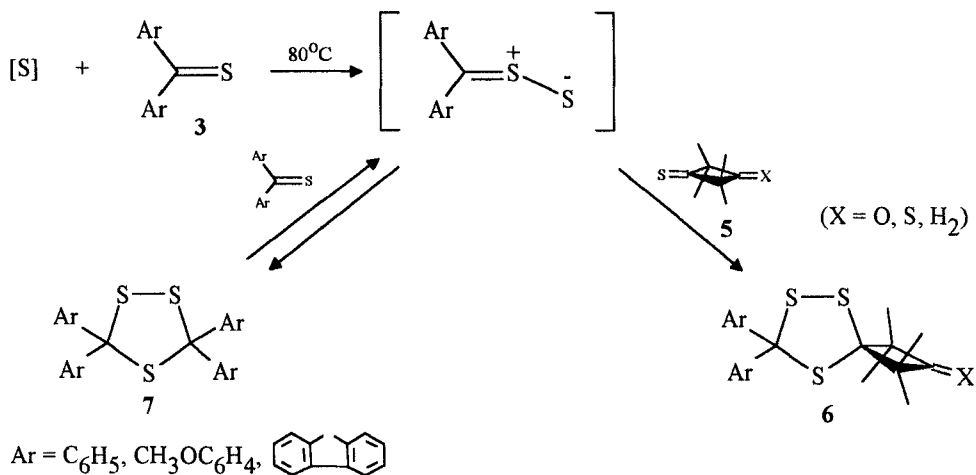
In contrast to the relatively stable sulfine compounds¹⁾, thiosulfines are not isolable and they appear only as intermediates which can be trapped using suitable dipolarophiles²⁻⁴⁾.



Huisgen and Rapp²⁾ reported on a smooth desulfurization of aryl substituted thiiranes by thiobenzophenone in which intermediate thiobenzophenone-S-sulfide added at room temperature to unconsumed thione to give 3,3,5,5-tetraphenyl-1,2,4-trithiolane. The latter was isolated as a crystalline substance in almost quantitative yield.



Now we report on the formation of thiosulfines at elevated temperature (80°C) in a three component system including thioketones **3** and **5** dissolved in phenyl azide (molar ratio of **3** and **5** 2:1). Aromatic thiones are known to react with 1,3-dipoles much faster than other dipolarophiles⁶⁾, so the first step of conversion must be the formation of an unstable 1,2,3,4-thiatriazoline **4** from aromatic thioketone **3** and phenyl azide.



Two-fold extrusion of nitrogen and elemental sulfur follows the preliminary step. Atomic sulfur is effectively intercepted by thioketones and in this way reactive thiosulfines are generated. The reaction time depended strongly on the nature of aromatic thione and in the case of the most reactive thiofluorenone conversion was completed within several minutes.

Sterical hindrance in the mixed trithiolanes **6** enhances the stability of this heterocyclic system and enables its isolation from reaction mixtures warmed up to 80°C. Tetraaryl trithiolanes **7** are thermally unstable²⁾ and this is the reason why Schönberg and Urban⁵⁾ were not successful in isolation of them when aromatic thiones and phenyl azide were heated at 80°C. In this reactions only N-phenyl imines of the corresponding carbonyl compound were observed as the products.

Acknowledgement G.M. thanks the Polish Committee for Scientific Research for financial support (KBN-Grant No. 2P 303 058 05) and H. H. thanks the Swiss National Science Foundation and F. Hoffmann - LaRoche AG, Basel, for financial support.

REFERENCES

1. B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 1;
B. Zwanenburg, *Phosphorus, Sulfur and Silicon* **1989**, *49*, 1.
2. R. Huisgen, J. Rapp, *J. Am. Chem. Soc.*, **1987**, *109*, 902.
3. A. Senning, H. C. Hansen, M. F. Abdel-Megeed, W. Mazurkiewicz, B. Jensen, *Tetrahedron* **1986**, *42*, 739.
4. T. Saito, Y. Shundo, S. Kitazawa, S. Motoki, *J. Chem. Soc., Chem. Commun.*, **1992**, 600.
5. A. Schönberg, W. Urban, *J. Chem. Soc.*, **1935**, 530.
6. R. Huisgen, E. Langhals, *Tetrahedron Lett.*, **1989**, *30*, 5369.