

This article was downloaded by:

On: 28 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>

α -Oxosulfines: New Generation Methods and Reactivity

Giuseppe Capozzi; Alessandra Corti; Stefano Menichetti; Cristina Nativi

To cite this Article Capozzi, Giuseppe , Corti, Alessandra , Menichetti, Stefano and Nativi, Cristina(1997) ' α -Oxosulfines: New Generation Methods and Reactivity', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 120: 1, 317 — 318

To link to this Article: DOI: 10.1080/10426509708545527

URL: <http://dx.doi.org/10.1080/10426509708545527>

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.

α -Oxosulfines: New Generation Methods and Reactivity

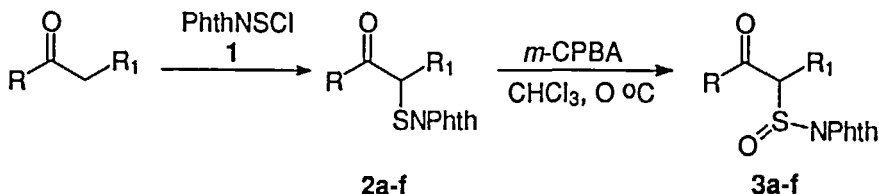
GIUSEPPE CAPOZZI, ALESSANDRA CORTI, STEFANO MENICHETTI*,
 CRISTINA NATIVI

*Centro C.N.R. "Chimica dei Composti Eterociclici", Dipartimento di Chimica
 Organica, Universita' di Firenze, Via.G. Capponi 9, I-50121, Firenze, Italy.*

Abstract. α -oxothiophthalimides **2** can be oxidised the corresponding sulfinimides **3** with *m*-chloroperoxybenzoic acid. Derivatives **3** in the presence of catalytic amount of pyridine generate the α -oxosulfines **4** which can be trapped by diene **5** to give dihydrothiopyranes **6** as mixture of diastereoisomers. The method appears simple and general since alkyl, aryl and hetroaryl substituted thiophthalimides can be fruitfully used.

We have reported that the reaction of phthalimidesulphenyl chloride **1** (PhthNSCl) with ketones affords α -oxothiophthalimides **2** which are simple precursors of the corresponding α -oxothiones¹. Thioketones can be generated by action of weak bases (like pyridine or lutidine) and trapped with 1,3-dienes, in classical Diels-Alder reactions, to give dihydrothiopyran systems¹.

We have now investigated the oxidation of derivatives **2** since the corresponding α -oxothiophthalimide-S-oxides appear as the precursors of α -oxosulfines. Treatment of sulfenamides **2a-f** with one equivalent of *meta*-chloroperoxybenzoic acid (*m*-CPBA) in chloroform at 0 °C affords the sulfinimides **3a-f** which were purified by trituration with cold ether (Scheme 1).



2a, 3a : R = Me ; R₁ = H

2d, 3d : R = 1-Naphthyl ; R₁ = H

2b, 3b : R = Ph ; R₁ = H

2e, 3e : R = 1-Thienyl ; R₁ = H

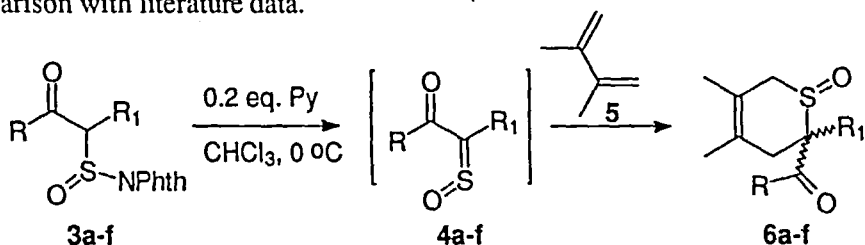
2c, 3c : R = 2-Naphthyl ; R₁ = H

2f, 3f : R = Ph ; R₁ = Me

SCHEME 1

Oxo-thiophthalimide-S-oxides **3a-f** are indeed able to generate the corresponding α -oxosulfines **4a-f** by treatment with catalytic amount of pyridine at $-20 \div 0^\circ\text{C}$.

When this reaction is performed in the presence of two equivalents of 2,3-dimethyl-1,3-butadiene **5** we isolated the cycloadducts **6a-f** as mixtures of distereoisomers (Scheme 2). The structure of derivatives **6b** and **6d** has been also unambiguously confirmed by comparison with literature data.²



Cycloadduct	R	R ₁	Cis/Trans ^a	Yield(%) ^b
6a	Me	H	47/53	65
6b	Ph	H	46/54	61
6c	2-Naphthyl	H	20/80	84
6d	1-Naphthyl	H	21/79	98
6e	2-Thienyl	H	10/90	56
6f	Ph	Me	> 2/98	45 ^c

a By ^1H NMR on the crude reaction mixture.

b Isolated yield of the mixture of diastereoisomers.

c Two equivalents of pyridine.

SCHEME 2

As shown in Scheme 2 this methods is useful for the formation of a wide range of thione-S-oxides since tolerates alkyl, aryl and heteroaryl substituted ketones. Due to its simplicity and to the mildness of the reaction conditions this new procedure appears as an interesting tools for the study of these reactive intermediates.

Moreover we demonstrated that α -oxothioaldehyde-S-oxides **4a-e** can also act as electron poor dienes in inverse electron demand Diels-Alder reactions with ethyl vinyl ether, thus increasing the synthetic utility of these heterocumulated species.

REFERENCES

1. G. Capozzi, S. Menichetti, C. Nativi, A. Rosi, and G. Valle, *Tetrahedron*, **48**, 9023, (1992).
2. G. B. Lenz, G. B.; H. Regeling, H. L. M. van Rozendaal, and B. J. Zwanenburg, *J. Org. Chem.* **50**, 2930 (1985).