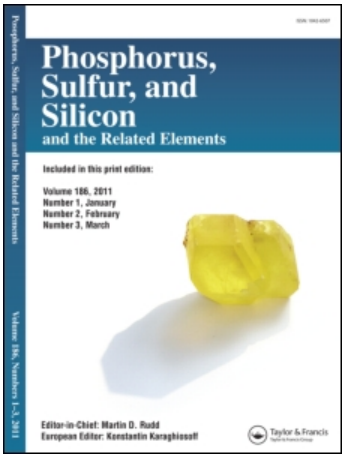

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

α-Oxosulfines: New Generation Methods and Reactivity

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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

Phosphorus, Sulfur, and Silicon, 1997, Vol. 120 & 121, pp. 317–318
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α–Oxosulfines: New Generation Methods and Reactivity

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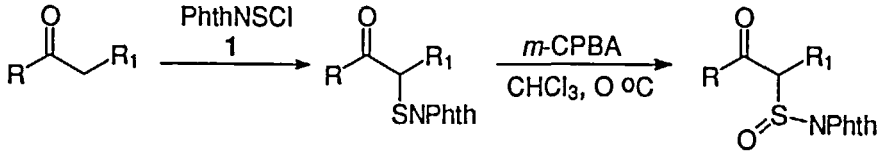
Abstract. α–oxothiophthalimides **2** can be oxidised the corresponding sulfinimides **3** with *m*-chloroperoxybenzoic acid. Derivatives **3** in the presence of catalytic amount of pyridine generate the α-oxosulfines **4** which can be trapped by diene **5** to give dihydrothiopyranes **6** as mixture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

We have reported that the reaction of phthalimidesulfenyl chloride **1** (PhthNSCl) with ketones affords α-oxothiophtalimides **2** which are simple precursors of the corresponding α-oxothiones[1]. 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 systems[1].

We have now investigated the oxidation of derivatives **2** since the corresponding α-oxothiophtalimide-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).



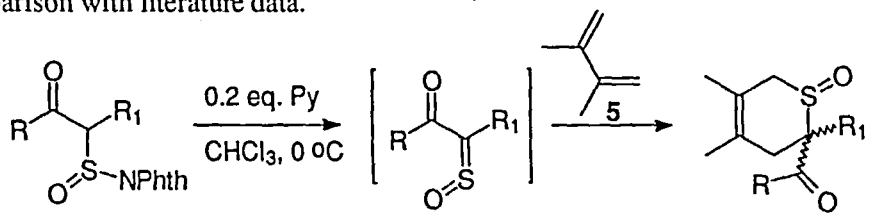
2a-f **3a-f**

2a, 3a : R = Me ; R_1 = H
2b, 3b : R = Ph ; R_1 = H
2c, 3c : R = 2-Naphthyl ; R_1 = H
2d, 3d : R = 1-Naphthyl ; R_1 = H
2e, 3e : R = 1-Thienyl ; R_1 = H
2f, 3f : R = Ph ; R_1 = Me

SCHEME 1

Oxo-thiophtalimide-S-oxides **3a-f** are indeed able to generate the corresponding α-oxosulfines **4a-f** by treatment with catalytic amount of pyridine at -20 ÷ 0 °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 pyridin.

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).