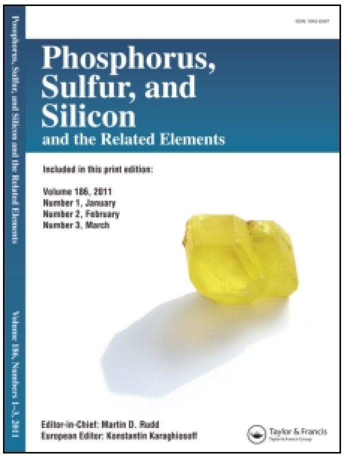
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Nucleophilic and Electrophilic Additions to Silylated Ketenimines Generated from Imidothioesters.

Christophe Fromont; Serge Masson

To cite this Article Fromont, Christophe and Masson, Serge(1997) 'Nucleophilic and Electrophilic Additions to Silylated Ketenimines Generated from Imidothioesters.', Phosphorus, Sulfur, and Silicon and the Related Elements, 120: 1, 397 — 398

To link to this Article: DOI: 10.1080/10426509708545566

URL: http://dx.doi.org/10.1080/10426509708545566

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.

Phosphorus, Sulfur, and Silicon, 1997, Vol. 120 & 121, pp. 397–398
Reprints available directly from the publisher
Photocopying permitted by license only

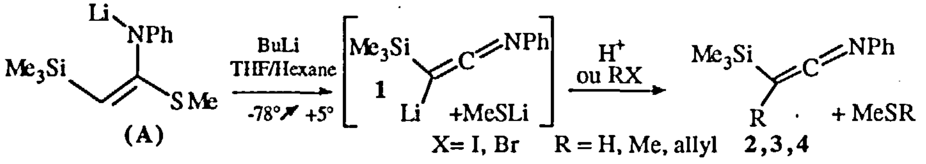
Nucleophilic and Electrophilic Additions to Silylated Ketenimines Generated from Imidothioesters.

CHRISTOPHE FROMONT AND SERGE MASSON*
Laboratoire de Chimie Moléculaire et Thio-organique, URA CNRS 480
ISMRA-Universté de Caen, F-14050 Caen, France.

The reactivity of stable silylated N-phenyl ketenimines towards some nucleophilic (organometallics, alcohols, thiols) and electrophilic reagents (PhSCl) were studied. Imino-coumarines (via tandem nucleophilic-electrophilic additions with Peterson olefination) and new phenylthio- and silyl-substituted ketenimines have been prepared.

INTRODUCTION :

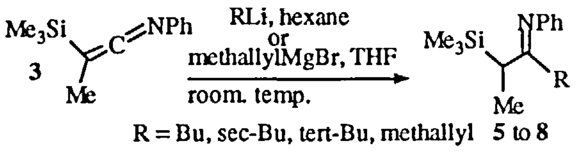
In a previous work we have shown that the reaction of 2 equivalents of butyllithium with the lithiated 2-trimethylsilylethanimidothioate (A), at temperatures higher than 0°C, leads to the silyl and lithium substituted ketenimine **1**. The latter, after protonation or alkylation, gives the stable silylated ketenimines **2**,**3** or **4**.[1]

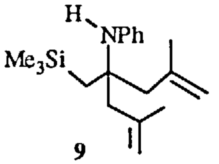


We present herein our first results related to the reactivity of these heterocumulenes, functionalised and stabilised by the trimethylsilyl substituent, towards some nucleophilic and electrophilic reagents.

RESULTS

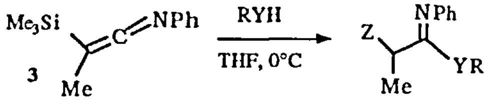
Although the electrophilic properties of the central carbon are reduced by the silylated substituent (as for silylated ketenes[2]), nucleophilic additions on this carbon were obtained at room temperature by the reaction of ketenimine **3** with organometallics such as BuLi, sec-BuLi, tert-BuLi and methallyl magnesium bromide. The expected imines **5-8** were thus isolated. From the non alkylated ketenimine **2**, a surprising double addition of the methallyl Grignard reagent led to the amine **9**.





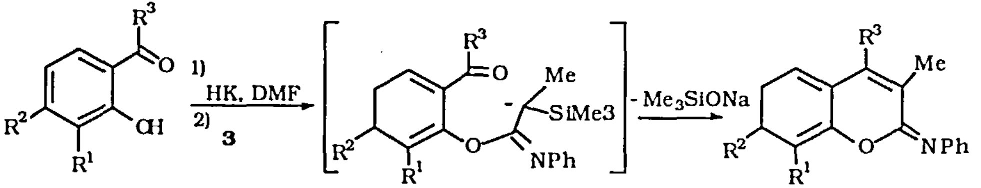
9

Additions of alcohols (catalyzed by Na or $ZnCl_2$) and thiols (in the presence of 1eq. of NEt_3) or lithium thiolates respectively led to the corresponding imidoesters **10-12** and imidothioesters **13-16**. However, in most cases, partial desilylation was observed except for the addition of Phenol ($ZnCl_2$), lithium benzenethiolate and tert-butylthiolate.



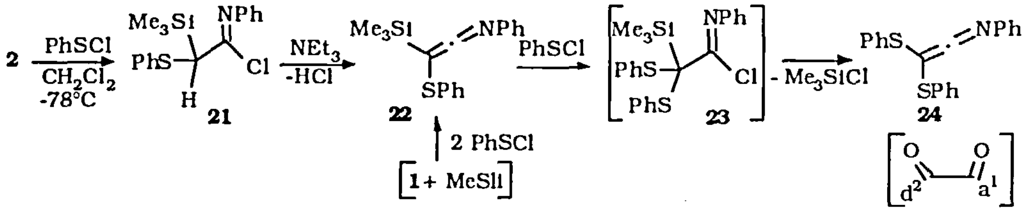
Y = O, R = Me, sec-Bu, tert-Bu **10-12**
Y = S, R = Me, Et, tert-Bu, Ph **13-16**
Z = Me_3Si or H

Tandem nucleophilic-electrophilic additions were observed by reaction of potassium salts of salicylic aldehydes or α-hydroxy acetophenones with ketenimine **3** in DMF. The addition on the central carbon is followed here by an intramolecular Peterson olefination leading to imino-coumarines **17-20**.

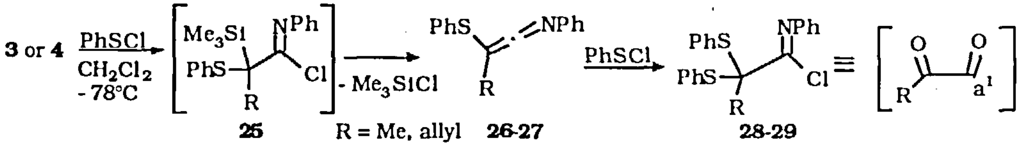


$[R^1, R^2, R^3 = H]$; $[R^1, R^3 = H, R^2 = OMe]$; $[R^1 = OMe, R^2, R^3 = H]$; $[R^1, R^2 = H, R^3 = Me]$ **17-20** (47 to 75%)

The addition of benzene sulfenyl chloride, good electrophilic reagent towards ketenimines[3] was then studied. Addition to the ketenimine **2** led to a stable imidoyl chloride **21** which was dechlorhydrated by NEt_3 into the phenythio substituted silylated-ketenimine **22**. The latter was also obtained in good yield (75% after distillation) by *in situ* addition of PhSCl to the lithiated ketenimine **1**. A second addition of PhSCl to ketenimine **22** led to the unstable imidoyl chloride **23** which spontaneously eliminates Me_3SiCl to give the bis-phenylthio substituted ketenimine **24** (a^1d^2 dicarbonyl synthon).



Reaction of the alkylated ketenimine **3** or **4** with PhSCl, also led to an unstable imidoyl-chloride **25** which produced the stable methyl-phenylthio ketenimines **26** or **27**. A double addition was again possible leading to the imidoyl chlorides **28-29**.



REFERENCES

1) N. Lage, S. Masson and A. Thuillier, *J. Chem. Soc., Perkin Trans. I*, 3389 (1991).
2) A. D. Allen, I. Egle, R. Janoschek, H. W. Liu, J. Ma, R. M. Marra and Th. T. Tidwell, *Chemistry Letters*, 45 (1996).
3) D. G. McCarthy, P. O. McCutcheon and D. P. Sheehan, *J. Chem. Soc. Perkin Trans. I*, 2899 (1994) and cited references.