Corrigendum

The following communication is a corrected version of one which appeared in *J. Chem. Soc., Perkin Trans 1*, 1991, 2269. The earlier version contained a transposed paragraph.

Synthesis of Silylated Ketenimines from a Metallated N-Phenyl α-Trimethylsilyl Imido Thioester

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Lithiated methyl N-phenyl-2-trimethylsilylethanimidothioate is regioselectively C-alkylated at −78 °C but, at a higher temperature in the presence of 1 equiv. of butyllithium, it is converted into a lithiated ketenimine which can be protonated or alkylated to give new and stable silylated ketenimines

Our previous work concerning the reactivity of metallated imido thioesters [1] has shown that the regioselectivity of their alkylation, at low temperatures, is sensitive to the nature of the R[1] group (Scheme 1). The alkylation occurs at the nitrogen atom when R[1] is an alkyl substituent and at the α-carbon atom when R[1] is a phenyl or a vinyl group involving a greater delocalization of the negative charge. Moreover, at higher temperatures, the metallated imido thioester (lithium or magnesium methylthio enaminate), in the presence of organometallics (R[2]Li or R[2]MgX), leads to imines resulting formally from a substitution of the methylthio group by R[2]. This was interpreted (Scheme 1) as the result of the elimination of MeSLi
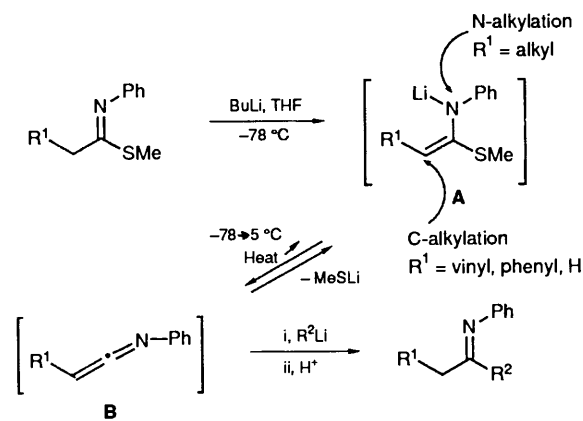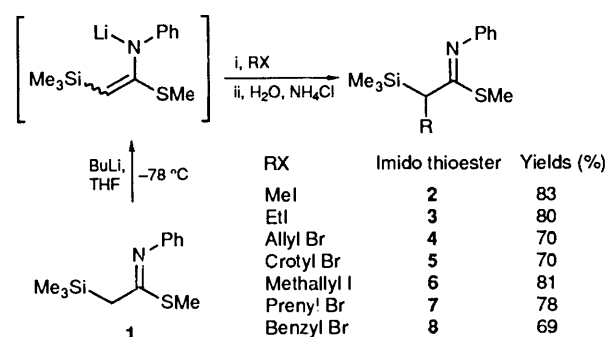

Scheme 1

leading to the formation of an equilibrium between the enaminate A and the ketenimine B.[2,3] This heterocumulene then undergoes a nucleophilic attack of the carbanionic part of the organometallic (R[2]) at its central carbon atom. However, in these reactions such an intermediate ketenimine was not isolated.

A study of the reactivity of metallated methyl N-phenyl-2-trimethylsilylethanimidothioate 1 presented herein firstly shows the influence of the trimethylsilyl group towards the regioselectivity of the alkylation at −78 °C and secondly confirms the existence, at higher temperatures of the assumed equilibrium by the obtention of new stable silylated ketenimines.

The silylated imido thioester 1 was prepared from trimethylsilylmethylmagnesium chloride and phenyl isothiocyanate.[4] The metallation of 1 by butyllithium and the addition of the alkylating agent was performed in THF at −78 °C. The temperature was then allowed to warm slowly to 20 °C and the

RX	Imido thioester	Yields (%)
MeI	2	83
EtI	3	80
Allyl Br	4	70
Crotyl Br	5	70
Methallyl I	6	81
Prenyl Br	7	78
Benzyl Br	8	69

Scheme 2

new α-silylated imido thioesters 2–8 were isolated in 70–83% yield (Scheme 2). No product resulting from an N-alkylation was detected. This demonstrates that the alkylation is selectively orientated towards the C-alkylation by the trimethylsilyl group.

In contrast, when 2 equiv. of butyllithium were added for the metallation at −78 °C, and the reaction mixture allowed to warm to *ca.* 5 °C before the addition of 2 equiv. of alkyl or allylic halides, the silylated ketenimines 10–14 were isolated in 55–74% yield (Scheme 3 and Table 1). These were sufficiently stable to be purified by flash distillation.

Formation of these new silylated heterocumulenes can be rationalized by the initial formation of the lithiated enaminate C at −78 °C and with warming, the silylated ketenimine 9 is formed. Then, due to the presence of the second equivalent of BuLi and to the carbanion stabilizing effect of the trimethylsilyl group, the deprotonation of the ketenimine 9 occurs (instead of the addition of BuLi as observed previously when R[1] = alkyl). This shifts the equilibrium towards the formation of the lithiated and silylated ketenimine D which is then regioselectively C-alkylated.† The second equivalent of halide used in these reactions, alkylated MeSLi and this avoids a

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† Generally the IR spectrum of the crude ketenimine obtained by this pathway, presents, beside the strong band at 2000 cm⁻¹, a smaller band at 2140 cm⁻¹. This can be attributed to the formation of a silylated ynamine resulting from the protonation or alkylation on the nitrogen of the N-lithiated ynamine form of the intermediate D. In some cases, the silylated ynamines was also detected by ¹H NMR and their formation did not exceed 12%. However, after flash distillation, the ketenimines only were isolated.

Table 1 Yields and ^{13}C NMR characteristics of $(Me_3Si)(R)C^a=C^b=NPh$

Ketenimine	R	Yield (%)	δC^a	δC^b
9	H	83	37.35	181.16
10	Me	74	46.86	183.58
11	Et	55	55.58	183.75
12	$CH_2=CHCH_2$	66	52.78	183.90
13	$MeCH=CHCH_2$	66	52.89	183.54
14	$PhCH_2$	57	56.13	184.33

Scheme 3
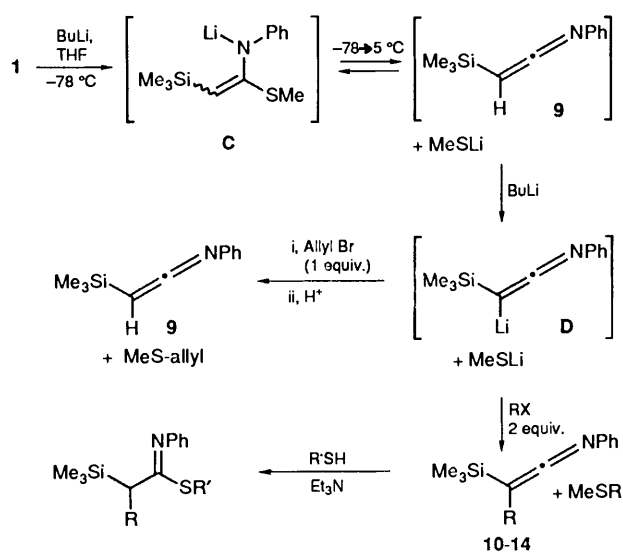
partial addition of MeSH to the ketenimines at the hydrolysis step.*

The replacement of alkylation by protonation allowed us to obtain the ketenimine **9** together with *ca.* 20% of the starting imido thioester **1**. The formation of **1**, which very probably results from the addition of methanethiol to the ketenimine **9** at the hydrolysis step, was minimized by the addition, at low temperature, of only 1 equiv. of alkylating agent (allyl bromide gave the best result) before hydrolysis. This can be rationalized by a selective allylation of MeSLi at −20 °C without any significant allylation of the lithiated ketenimine **D**. Under these

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* We indeed observed that thiols readily add to the silylated ketenimines to give imido thioesters, but some desilylation occurs. This desilylation can be minimized by using the trimethylammonium salts of the thiols.

† From the methyl N-phenyl-2-phenylethanimidothioate, we have already been able to obtain, *via* the corresponding lithiated ketenimine, the corresponding N-phenyl(methyl)phenylketenimine [N-(2-phenyl-propenylidene) aniline].

conditions, the ketenimine **9** was isolated in a 80% yield after flash distillation.

These silylated heterocumulenes are new potential intermediates in organic synthesis and their reactivity will be examined. In particular, the lithiated silylated ketenimine **D** could possibly be compared to the phosphaketenimine ylide [N-phenyl(triphenylphosphoranylidene)ethenimine] which is a useful synthetic tool described by Bestmann.[5] We are also at present studying the generality of this new route to ketenimines starting from imido thioesters substituted at the α-position by other carbanion stabilizing groups.†

References

1 S. Masson, V. Mothes and A. Thuillier, *Tetrahedron*, 1984, **40**, 1573.
2 M. El Jazouli, S. Masson and A. Thuillier, *J. Chem. Soc., Chem. Commun.*, 1985, 1598.
3 M. El Jazouli, N. Lage, S. Masson and A. Thuillier, *Bull. Soc. Chim. Fr.*, 1988, **5**, 883.
4 P. Gosselin, S. Masson and A. Thuillier, *Tetrahedron Lett.*, 1978, **30**, 2715.
5 H. J. Bestmann, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 349.