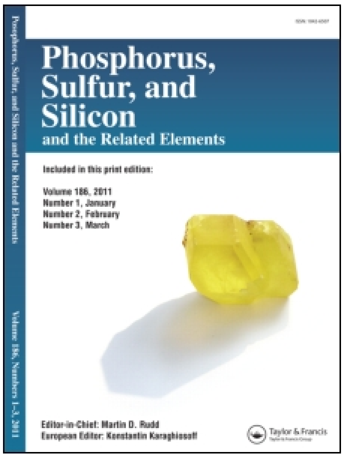

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CARBON-CARBON BOND FORMATION AND KETENIMINE SYNTHESIS FROM N-PHENYL IMIDOTHIOESTERS

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CARBON-CARBON BOND FORMATION AND KETENIMINE SYNTHESIS FROM N-PHENYL IMIDOTHIOESTERS.

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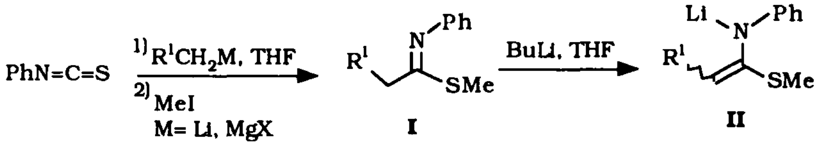
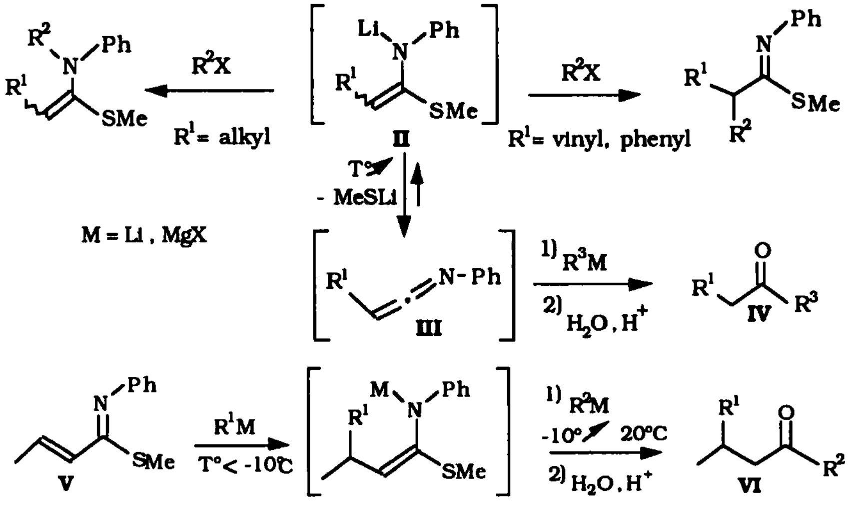
Abstract: Methyl N-phenyl ethanimidothioate **1** and its α-silylated homologue **2** are metallated into lithiated enaminates which can be regioselectively monoalkylated at -78°C on the α-carbon atom. Imidothioester **2**, treated at higher temperatures by 2 equivalents of Buli, leads, after alkylation or hydrolysis, to stable silylated N-phenyl ketenimines. Formation of ketenimines are also observed by flash thermolysis of **2** or of the silylated S,N-ketene acetal **10**.

N-phenyl imidothioesters (I), precursors of dithioesters, thiolesters and amides are readily prepared by the reaction of organolithium or magnesium compounds with phenylisothiocyanate [1,2] followed by methylation.



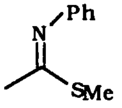
Our previous work concerning the reactivity of metallated imidothioesters (lithiated enaminates II) has already shown that the regioselectivity of their alkylation is sensitive to the nature of the R^1 group. At low temperatures, the alkylation of II occurs regioselectively either at the nitrogen (R^1= alkyl) or at the carbon atom (R^2= vinyl, phenyl). Moreover, at higher temperatures, the enaminates II are assumed to give the ketenimines III which were characterized by their trapping with organometallics. This reaction allows the synthesis of ketones (IV) via their corresponding imines [3]. From an α, β-ethylenic imidothioester (V), this trapping associated with a 1,4-addition allows a one pot 1,3-addition of two different alkyl chains and this was used for the synthesis of non-symmetrical and isoprenic ketones (VI) [4].



We present in this communication :

- *new results concerning the regioselective alkylation on the α carbon atom* of N-phenylethanimidothioate **1** and of N-phenyl trimethylsilyl ethanimidothioate **2**,

- *a new synthetic route to stable silylated ketenimines* (potentially useful synthons) from the imidothioester **2**. This result and two flash thermolysis experiments, from **2** and from a silylated S,N-ketene acetal, also confirm the assumed formation of intermediate ketenimines in our previous work [3].



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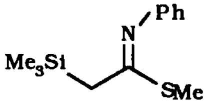
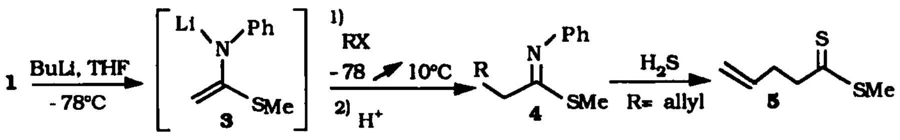


2

The silylated imidothioester **2** was prepared by the usual method starting from trimethylsilylmethylmagnesium chloride.

A) ALKYLATION OF ETHANIMIDOTHIOATE 1

In somewhat surprising contrast to its homologue **II** (R^1= alkyl), the lithiated enaminate **3** derived from **1** was C-alkylated with alkylic and allylic iodide or bromide leading to imidothioesters **4**.

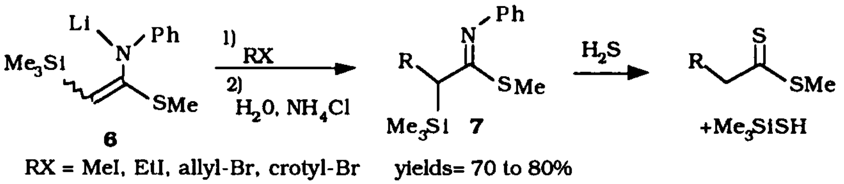


R= MeI, EtI, allyl-Br, crotyl-Br, methallyl-Br Yields= 65 to 83%

This reaction allows, in particular, the preparation of γ-ethylenic imidothioesters or dithioesters (after sulfhydrolysis) such as **5**. The lack of inversion of the allylic chain with crotyl bromide is strongly in favour of a direct alkylation at the carbon instead of an alkylation at the nitrogen followed by a [3,3] sigmatropic rearrangement.

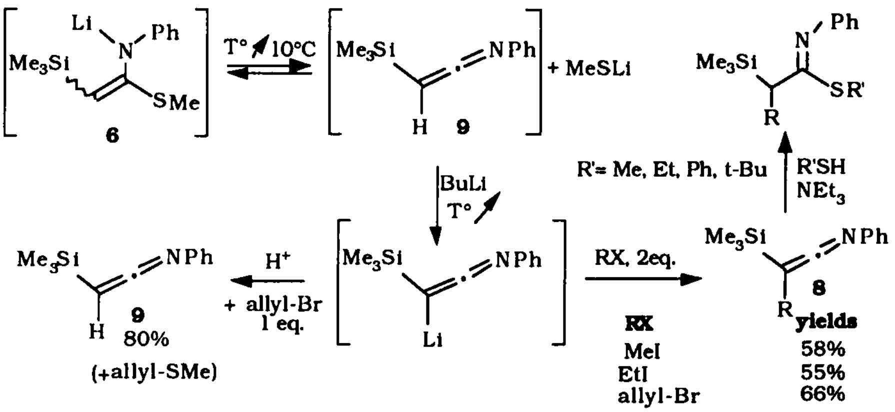
B) C-ALKYLATION OF TRIMETHYLSILYLETHANIMIDOTHIOATE 2.

The C-alkylation observed with the lithiated enaminate **6** shows that the regioselectivity is orientated by the carbanion stabilizing effect of the trimethylsilyl group. Treated at -78°C by iodomethane, iodoethane, alkyl or crotyl bromide, enaminate **6** led to the new α-silylated imidothioesters **7** in 70 to 80 % yields. These are very sensitive to acidic medium and cannot be sulfhydrolyzed into the corresponding dithioesters without desilylation.



C) SYNTHESIS OF STABLE SILYLATED KETENIMINES FROM IMIDOTHIOESTER 2.

When, before the addition of the alkylating agent, the silylated intermediate **6** was allowed to warm to about +10°C in the presence of 1 equiv. excess of butyllithium, instead of the silylated imidothioesters **7**, new alkyl trimethylsilyl ketenimines **8** were isolated in 55 to 66 % yields after short path distillation.



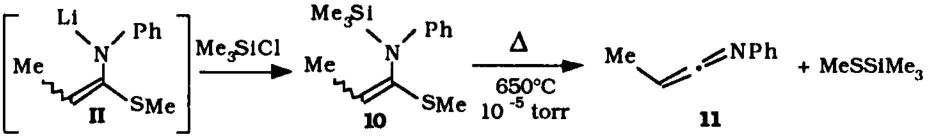
This result can be rationalized, starting from the enaminate **6** initially formed at low temperature, by an elimination of lithium methyl thiolate leading to ketenimine **9**.

The assumed equilibrium between **6** and **9** is shifted by lithiation of **9** and then alkylation leads to ketenimines **8**. These last compounds were characterized by IR (ν = 2000 cm^{-1}), ^{13}C and ^{1}H NMR spectroscopy and by their reactions with thiols which led back to imidothioesters.

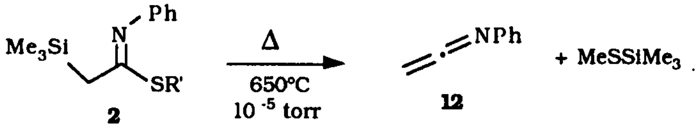
When the alkylation was replaced by protonation, the N-phenyl trimethylsilyl ketenimine **9** (not previously described) was isolated. The better yield (80 %) was obtained when 1 equiv. of allyl bromide was added before the hydrolysis. A selective allylation of MeSLi liberated in the reaction presumably avoids a partial addition of MeSH to the ketenimine at the protonation stage, reaction which leads back to the starting imidothioester.

D) KETENIMINE FORMATION BY FLASH VACUUM THERMOLYSIS OF A N-SILYLATED KETENE S,N-ACETAL 10 AND OF SILYLATED IMIDOTHIOESTER 2.

N-Silylation of the metallated imidothioate **II** (R^1= Me) leads to the corresponding ketene S, N-acetal **10** [2]. Flash vacuum thermolysis of this compound led mainly to the elimination of Me_3SiSMe and the formation of the methyl ketenimine **11** characterized by low temperature infra-red and ^{13}C-NMR spectra.



When silylated imidothioester **2** was thermolysed under the same conditions the N-phenyl ketenimine **12** was also identified by low temperature spectroscopy.



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