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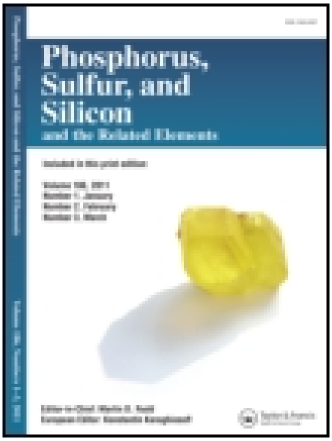

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# Nucleophilic and Electrophilic Additions to Silylated Ketenimines Generated from Imidothioesters.

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# Nucleophilic and Electrophilic Additions to Silylated Ketenimines Generated from Imidothioesters.

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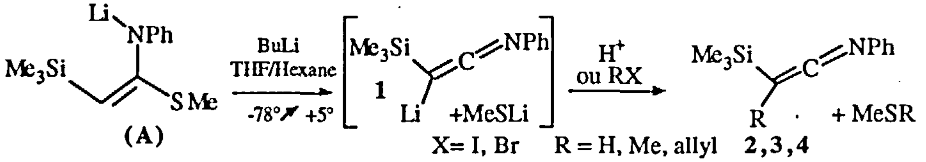
The reactivity of stable silylated N-phenyl ketenimines towards some nucleophilic (organometallics, alcohols, thiols) and electrophilic reagents (PhSCl) were studied. Imino-coumarines (via tandem nucleophilic-electrophilic additions with Peterson olefination) and new phenylthio- and silyl-substituted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

## INTRODUCTION :

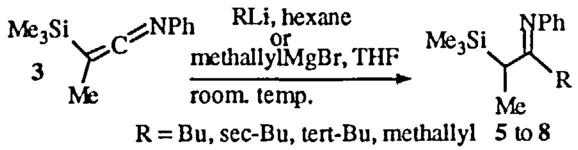
In a previous work we have shown that the reaction of 2 equivalents of butyllithium with the lithiated 2-trimethylsilylethanimidothioate (A), at temperatures higher than 0°C, leads to the silyl and lithium substituted ketenimine 1. The latter, after protonation or alkylation, gives the stable silylated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

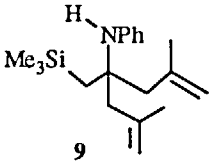


We present herein our first results related to the reactivity of these heterocumulenes, functionalised and stabilised by the trimethylsilyl substituent, towards some nucleophilic and electrophilic reagents.

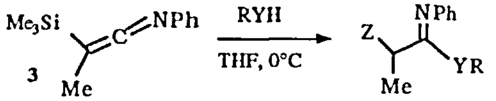
## RESULTS

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.



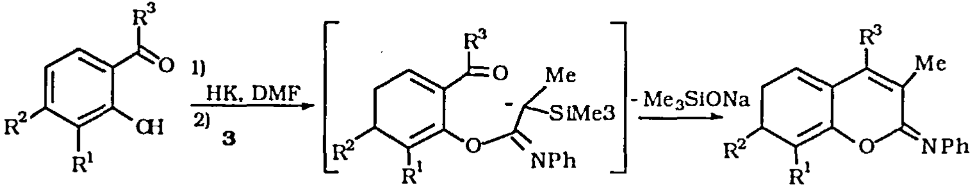


Additions of alcohols (catalyzed by Na or $ZnCl_2$) and thiols (in the presence of 1eq. of $NEt_3$) or lithium thiolates respectively led to the corresponding imidoesters 10-12 and imidothioesters **13-16**. However, in most cases, partial desilylation was observed except for the addition of Phenol ($ZnCl_2$),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



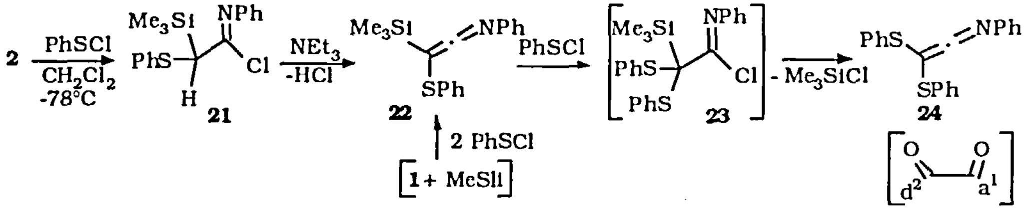
Y = O, R = Me, sec-Bu, tert-Bu **10-12**
Y = S, R = Me, Et, tert-Bu, Ph **13-16**
Z = $Me_3Si$ or H

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**.

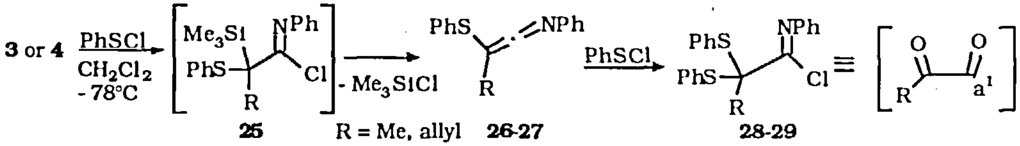


[$R^1$, $R^2$, $R^3$ = H]; [$R^1$, $R^3$ = H, $R^2$ = OMe]; [$R^1$ = OMe, $R^2$, $R^3$ = H]; [$R^1$, $R^2$ = H, $R^3$ = Me] **17-20** (47 to 75%)

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**.



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