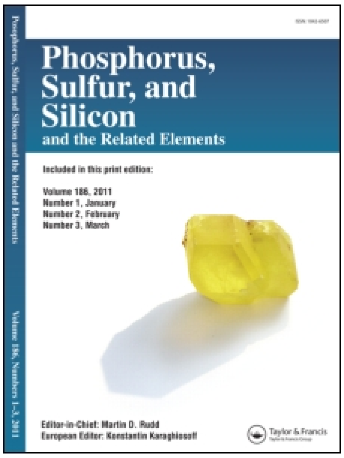

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A General Access to α,β-Acetylenic Thiocarbonyl Compounds

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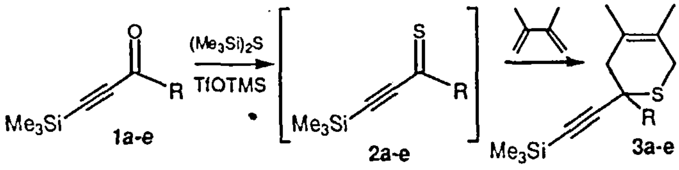
Reaction of several α,β-acetylenic carbonyl compounds with bis(trimethyl)silylsulfide/TfOTMS affords the first example for the synthesis of thioketones, thioacylsilane and thioaldehyde in the acetylenic series.

Keywords: alkynyl carbonyl compounds; thionation; cycloadditions

α,β-Unsaturated thiocarbonyl compounds are still a class of challenging molecules, some difficulties being still encountered in their synthesis, due to the possible formation of Michael type adducts. To overcome these problems, some protecting groups have been used and few methods have been reported for the synthesis of α,β-unsaturated thioketones in the ethylenic series[1] but, to the best of our knowledge, none in the acetylenic series.

With the aim to develop a general approach for the synthesis of alkynyl thiocarbonyl derivatives, we envisaged that the presence of an easily removable trimethylsilyl group on the triple bond could be beneficial to prevent undesirable addition to the enone moiety.

When we applied our reported procedure[2] for the thionation of β-silylpropynoyl trimethylsilane **1a** using bis(trimethylsilyl)sulfide (HMDST) in the presence of TfOTMS as catalyst, a smooth entry to the corresponding α,β-acetylenic thioacylsilane **2a** has been obtained, being isolated as its Diels-Alder cycloadduct 3a (Scheme 1).



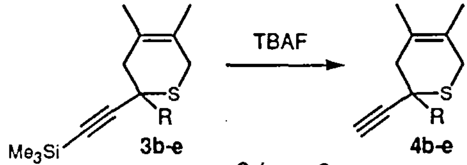
1a R = Me$_3$Si
1e R = H
1b R = CH$_3$
1c R = (CH$_2$)$_2$Cl
1d R = PhCH$_2$

Scheme 1

This methodology can be as well extended to the thionation of different alkynyl ketones **1b-d**, to afford a wide range of this new class of alkynyl thioketones **2b-d** (Scheme 1).

The HMDST based protocol was also used to obtain the first example of an acetylenic thioaldehyde **2e**, isolated as the 2-monosubstituted dihydrothiopyran adduct **3e** (Scheme 1).

As anticipated, when the so obtained β-silylated-α,β-acetylenic thioderivatives **3b-e** were treated in the presence of TBAF a general access to unsubstituted alkynyl thiocarbonyl compounds **4b-e** has been evidenced (Scheme 2), thus demonstrating the mildness and the generality of the described procedure.



Scheme 2

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