

Evaluation of C-trialkylsilyl enol and thioenol ethers as intermediates in the synthesis of acylsilanes

Catherine Hammaeher, Imad Ouzzane, Charles Portella* and Jean-Philippe Bouillon*,†

UMR 6519 'Réactions Sélectives et Applications', CNRS-Université de Reims Champagne-Ardenne, B. P. 1039, 51687 REIMS Cedex 2, France

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Abstract—C-silyl enol ethers or thioenol ethers have been prepared by a Peterson reaction, as intermediates for acylsilane synthesis. Bis(trialkylsilyl)(methoxy)- or -(methylsulfanyl)methanes bearing identical or different trialkylsilyl groups were used as starting materials in order to assess the selectivity of the Peterson elimination step. A good selectivity was observed only with ethers bearing the TMS and TBDMS groups. However, there is no practical interest to use such reagents owing to the difficulty to obtain them in correct yields. Bis(trimethylsilyl)(methylsulfanyl)methane proved to be a good reagent for the preparation of C-silyl thioenol ethers, which are hydrolyzed under classical acid conditions to give acylsilanes in fair overall yields. This convenient procedure was extended to the synthesis of bis(acylsilanes).

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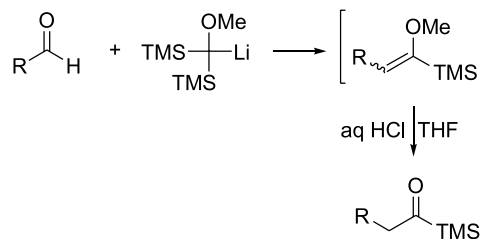
1. Introduction

Acylsilanes are interesting compounds exhibiting specific properties beside the usual ones of carbonyl derivatives.¹ The interest of their chemistry is strongly dependant on their more or less easy synthesis. Several strategies were reported, starting from compounds as various as aldehydes,^{2,3} esters,⁴ acyl chlorides,⁵ alkyl halides or triflates,⁶ epoxides,⁷ diols,⁸ and others. One of the more general methods, proposed simultaneously by Brook's and Corey's groups,² is based on the reversed polarity (umpolung) concept and uses dithioacetals as key intermediates. First developed essentially via the thioacetalization of aldehydes as starting materials, the methodology was further extended to the alternative approach using alkylation of 2-lithio-2-trimethylsilyldithiane as silylcarbonyl moiety equivalent.^{6–8} These dithioacetal routes are very useful, and they were involved in the preparation of a wide range of acylsilanes, including functionalized acylsilanes and bis(acylsilanes).^{6–8}

The dithioacetal methodology suffers some drawbacks inherent to the last step of carbonyl releasing, which

needs oxidative hydrolytic conditions. Even if one can avoid the mercury salts initially proposed, the conditions are not trivial and not compatible with various functional groups. On the other hand, aldehydes are starting materials of choice, a lot of them being commercially available. Very few attention has been paid to other methods of preparation of acylsilanes from aldehydes. The one reported by Yoshida and co-workers³ seems to have not been exploited much.⁹ Based on a Peterson reaction, this method is interesting because the last step requires classical hydrolytic conditions (Scheme 1).

Being involved in some aspects of the chemistry of acylsilanes, especially functionalized ones, we were interested in a possible extension of this 'Peterson' approach. Our goals were to investigate the building blocks described in Scheme 2, as precursors of C-trialkylsilyl enol or thioenol ether type intermediates. Our interest for bis(acylsilanes) prompted us to also investigate a possible selectivity in the

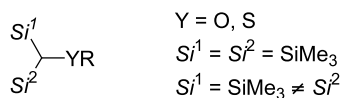


Scheme 1.

Keywords: Organosilicon; Peterson olefination; Acylsilane; Enol ether; Thioenol ether.

* Corresponding authors. Tel.: +33 32 691 3234; fax: +33 32 691 3166 (C.P.); e-mail addresses: charles.portella@univ-reims.fr; jean-philippe.bouillon@univ-rouen.fr

† Present address: Sciences et Méthodes Séparatives-EA 3233, Université de Rouen. IRCOF. F-76821 Mont-Saint-Aignan Cedex, France.



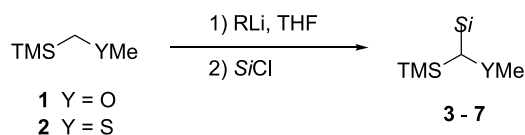
Scheme 2.

Peterson elimination step by differentiating the two trialkylsilyl groups.

2. Results and discussion

2.1. Synthesis of the bis(silylated) building blocks

The procedure and results are depicted in Scheme 3 and Table 1. The methoxy derivatives **3–5** have been prepared by applying to methoxymethyl(trimethyl)silane **1** the metallation–silylation sequence reported by Yoshida's group.³ The reaction works well for bis(trimethylsilyl)-(methoxy)methane **3** as reported by Yoshida, but proved to be more difficult with (*tert*-butyl)dimethylsilyl (TBDMS) derivative **4**. Surprisingly, a better yield was obtained for the tris(isopropylsilyl) (TIPS) derivative **5**.



Scheme 3.

Table 1. Preparation of bis(silylated) building blocks **3–7**

Y	RLi	Si ^a	Product (%)
O	<i>s</i> -Bu	TMS	3 (85) ³
O	<i>s</i> -Bu	TBDMS	4 (28)
O	<i>s</i> -Bu	TIPS	5 (56)
S	<i>n</i> -Bu	TMS	6 (65) ¹¹
S	<i>n</i> -Bu	TBDMS	7 (62)

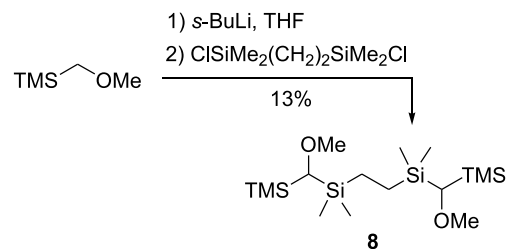
^a TMS = trimethylsilyl, TBDMS = (*tert*-butyl)dimethylsilyl, TIPS = tris(isopropylsilyl).

The bis(silylated) methylsulfonyl derivatives **6–7** were prepared from methylsulfonyl (trimethylsilyl)methane¹⁰ according to a similar procedure, except that the presence of sulfur allows to use *n*-butyllithium (Scheme 3). As for oxygen series, only the bis(trimethylsilyl) derivative **6** had already been prepared, for different purposes.¹¹ In contrast to the oxygen analogue, the TBDMS derivative **7** has been obtained in fairly good yield (Table 1).

Just as variously substituted silyl groups are introduced to assess a possible selectivity in the Peterson reaction, the tetrasilyl reagent **8** has been synthesized, though in poor yield, in order to investigate a possible application in bis(acylsilane) synthesis (Scheme 4).

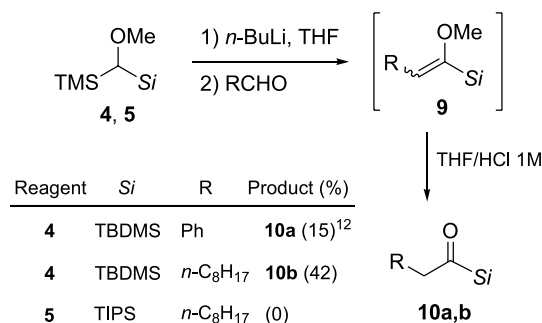
2.2. Peterson reaction using reagents **3–7**

To the best of our knowledge, the chemoselectivity of the elimination step of the Peterson olefination process had never been investigated on bis(silylated) organometallic species. One could expect that the intramolecular formation



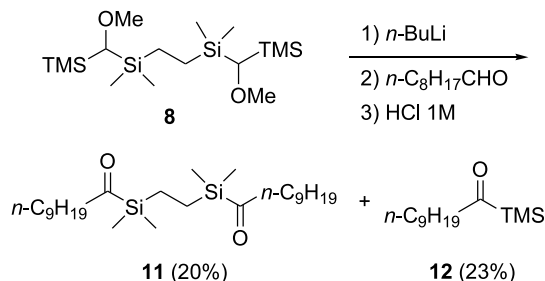
Scheme 4.

of the Si–O bond would be favoured with the less bulky TMS group. Indeed, when the reagent **4** is reacted with *n*-butyllithium and then with an aldehyde, a single acylsilane (**10a**¹² or **10b**) is isolated, albeit in low yield, after hydrolysis of the corresponding enol ether intermediate **9** (Scheme 5). No reaction was observed with the TIPS derivative **5** treated in the same conditions.



Scheme 5.

The steric hindrance around one silicon is a critical point since the reaction is no longer selective with the reagent **8**. In this case, the expected bis(acylsilane) **11** and decanoyl-trimethylsilane **12**¹³ are obtained in similar yields, owing to a too weak difference in the bulk around the silicon atoms (Scheme 6).



Scheme 6.

Except the bis(TMS) reagent **3**, which proved to be useful for acyl(trimethyl)silane synthesis,³ the oxygenated reagents **4**, **5** and **8** are definitely not convenient owing to the low yields at the successive stages of the synthesis (Schemes 5 and 6). Hence we turned our attention to the methylsulfonyl analogues (Scheme 7, Table 2). Reagent **6**, which had never been considered in Peterson reaction, reacts effectively with benzaldehyde to give a high yield of the thioenol ether **13a**, as a 58/42 *E/Z* diastereomers mixture (NOE determination). The reaction was applied to a series

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