REINVESTIGATION OF THE REACTION OF LITHIUM TRIMETHYLSILYL

ACETATE ENOLATE WITH CHLOROTRINETHYLSILANE

Moncef BELLASSOUED and Marcel GAUDEMAR

Université P. et M. Curie, Laboratoire de Synthèse Organométallique, 4, Place Jussieu, 75252 - PARIS Cedex 05 (France).

Reaction of lithium trimethylsilyl acetate enolate with chlorotrimethylsilane affords bis(trimethylsilyl) ketene acetal 1 or trimethylsilyl α -trimethylsilylated acetate 2 depending on the reaction conditions.

In 1972, Ainsworth and coll.¹⁻² have reported that $ClSiMe_3$ reacts at -78°C with lithium trimethylsilyl acetate in THF-hexane to give an equal amount of bis(trimethylsilyl) ketene acetal <u>1</u> and trimethylsilyl α -trimethylsilylated acetate <u>2</u>.

I
$$LiN(iPr)_2 \xrightarrow{1^{\circ})MeCO_2SiMe_3, -78^{\circ}C, 30 \text{ mn}} CH_2 \equiv C \xrightarrow{OSiMe_3} + CH_2CO_2SiMe_3$$

2') $ClsiMe_3, -78^{\circ}C \longrightarrow 25^{\circ}C \xrightarrow{OSiMe_3} SiMe_3$
1 2

The authors have also shown that the acyclic homologue esters lead exclusively to the corresponding bis(trimethylsilyl) ketene acetals, but did not offer any explanation for the formation of the mixture obtained from the first term. Since then, a few articles concerning the preparation of similar trimethylsilyl derivatives have been published³⁻⁵, but hardly any articles dealing with compounds 1 and 2. Nevertheless, the synthesis of 2 was carried out in an unequivocal manner⁶ whereas, to our knowledge, this is not the case of 1. In connection with our work on silicon derivatives, we show in this Letter how the reaction described previously by Ainsworth can be applied to provide exclusively compounds $\underline{1}$ or $\underline{2}$ and we try to explain the formation of these two products.

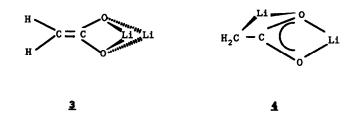
At the first, we have reproduced Ainsworth's experiment in THF-ether⁷, the solvent used throughout our work. We then obtained the same ratios of the mixture described by the author (I : 47 %; II : 53 %) in 66% yield. Thus, the co-solvent (hexane or ether) does not seem to play any role in the formation of the two isomers. However, trimethylsilyl α -trimethylsilylated acetate 2 is obtained solely in 82 % isolated yield when the lithiated trimethylsilyl acetate is left aside overnight at -70°C before trapping with ClSiMe₃⁷.

On the other hand, quenching the trimethylsilyl acetate lithium enolate immediately after its formation by ClSiMe₃ at -20°C/-10°C within 10 mn leads to the silyl ketene acetal 1 in moderate yield⁷ (Eqn. III). The formation of Claisen-type condensation products, difficult to avoid at that temperature, accounts for the moderate yield. In order to reduce these side reactions and to improve the yield of 1, we were tempted to add the mixture (Me₃CO₂SiMe₃ + ClSiMe₃) to LDA at a temperature lower than -20°C. Unfortunately, the lithiated acetate does not react at that temperature with $ClSiMe_3$ as we have shown previously⁹. We have also reported that sodium enolates, derived from ketones, react at -70°C with ClSiMe3 to give enethers⁹. Therefore, the sodium the kinetic **O-trimethylsilyl** trimethylsilyl acetate enolate should afford exclusively the trimethylsilyl ketene acetal 1 in good yield⁷ (Eqn. IV).

III
$$\operatorname{LiN}(\operatorname{iPr})_2$$

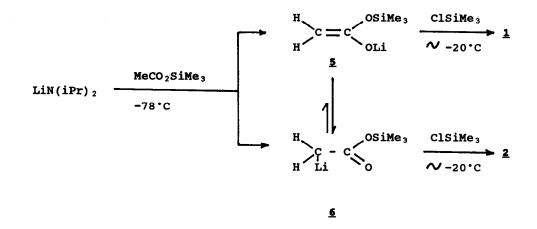
 $\xrightarrow{(\operatorname{MeCO}_2\operatorname{SiMe}_3 + \operatorname{ClSiMe}_3)}_{-20^{\circ}\mathrm{C} \longrightarrow -10^{\circ}\mathrm{C}, \ 10 \ \mathrm{mn}}$
IV $\operatorname{NaN}(\operatorname{SiMe}_3)_2$
 $\xrightarrow{1^{\circ}) \operatorname{MeCO}_2\operatorname{SiMe}_3, \ -70^{\circ}\mathrm{C}, \ 2 \ \mathrm{mn}}_{2^{\circ}) \operatorname{ClSiMe}_3, \ -70^{\circ}\mathrm{C} \longrightarrow 25^{\circ}\mathrm{C}}$
(yield : 47 %)
(yield : 47 %)
(yield : 79 %)

In other respects, a recent study about the structure of monomeric dilithiated acetic acid dianion has been reported by Schleyer and coll.¹⁰; the results of ab initio and semi-empirical MNDO calculations indicate $\underline{3}$ and $\underline{4}$ to be the most stable structures.



Moreover, Maroni and coworkers¹¹ have demonstrated by ¹³C-NMR and IR spectroscopy the O-metallated structure of lithium t-butyl acetate.

Thus, if we admit that silylation of enolates proceeds without modifying the structure of the anions¹², it is reasonable to speculate that **1** is formed from the corresponding enolate **5** and the trimethylsilyl α -silylated product **2** from the more stable C-lithiated intermediate <u>6</u>.



The mixture of compounds $\underline{1}$ and $\underline{2}$ obtained by Ainsworth can be then explained by a partial equilibration of $\underline{5}$. A change in the aggregation states of the enolate¹³ could be considered as an alternative explanation. For this, further studies on the structures of $\underline{5}$ and $\underline{6}$ using ¹³C-NMR and IR are underway.

References and notes

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- 7 The experiments are carried out in a mixture of 20 ml ether 20 ml THF. Phenanthrene is used as electron acceptor according to the method of Gaudemar⁸. For 0.1 at.g of Li or Na, we use 0.8 mol of MeCO₂SiMe₃ and 0.1 mol of ClSiMe₃. Then the precipitate is filtered off on Celite, the solvent removed under ambient pressure and the product distilled in vacuo. CH₂=C(OSiMe₃)₂ : b.p. 50°C/10 mm Hg ; Me₃SiCH₂CO₂SiMe₃ : b.p. 61°C/10 mm Hg.
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