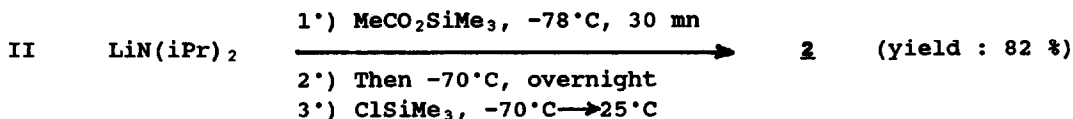
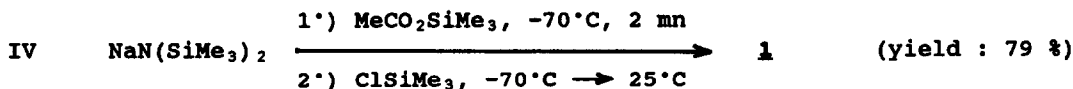
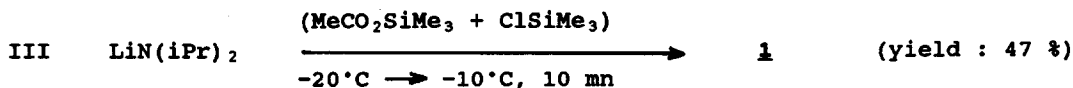


In connection with our work on silicon derivatives, we show in this Letter how the reaction described previously by Ainsworth can be applied to provide exclusively compounds **1** or **2** and we try to explain the formation of these two products.

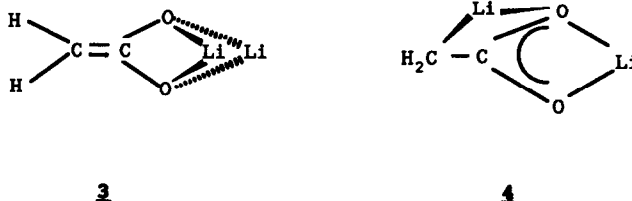
At the first, we have reproduced Ainsworth's experiment in THF-ether⁷, the solvent used throughout our work. We then obtained the same ratios of the mixture described by the author (I : 47 % ; II : 53 %) in 66% yield. Thus, the co-solvent (hexane or ether) does not seem to play any role in the formation 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 ClSiMe₃, as we have shown previously⁹. We have also reported that sodium enolates, derived from ketones, react at -70°C with ClSiMe₃ to give the kinetic O-trimethylsilyl enethers⁹. Therefore, the sodium trimethylsilyl acetate enolate should afford exclusively the trimethylsilyl ketene acetal **1** in good yield⁷ (Eqn. IV).

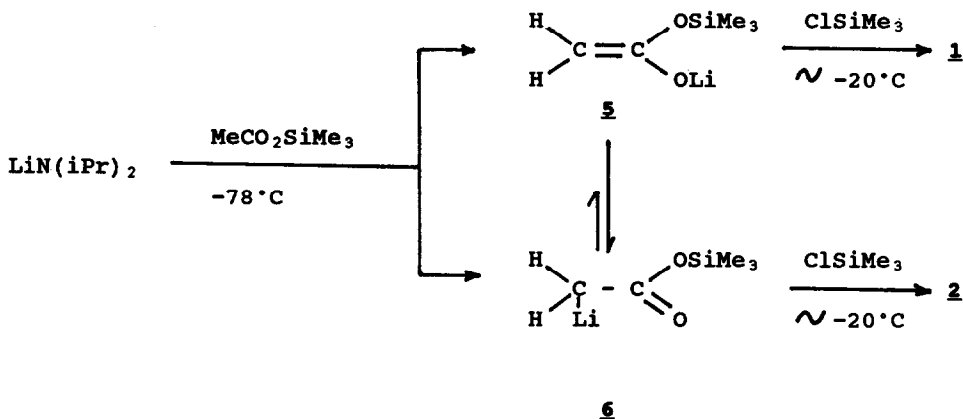


In other respects, a recent study about the structure of monomeric dilithiated acetic acid dianion has been reported by Schleyer and coll.¹⁰; the results of ab initio and semi-empirical MNDO calculations indicate **3** and **4** to be the most stable structures.



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 **6**.



The mixture of compounds **1** and **2** obtained by Ainsworth can be then explained by a partial equilibration of **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 **5** and **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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