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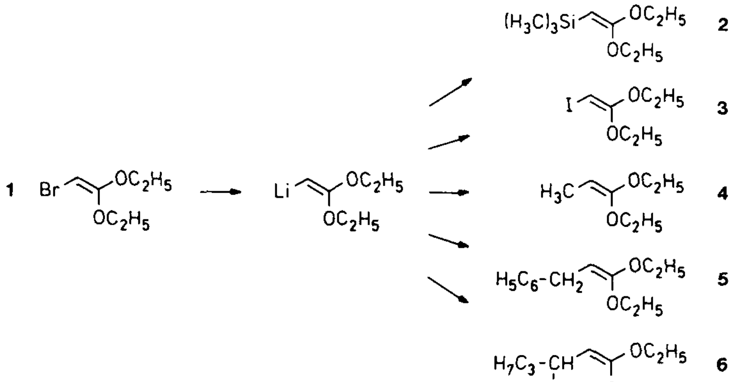
2,2-Di(ethoxy)vinyllithium : A Synthetic Equivalent of the Ethyl Acetate Anion

Heng-xu Wei and Manfred Schlosser *

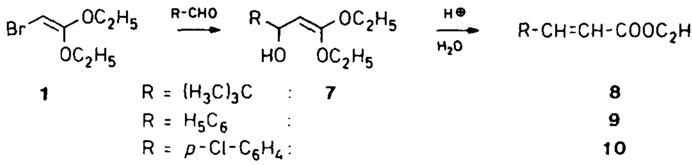
Institut de Chimie organique de l'Université
Bâtiment de Chimie (BCh), CH-1015 Lausanne-Dorigny, Switzerland

Abstract : 2,2-Diethoxyvinyllithium can be readily generated from 2-bromo-1,1-diethoxyethylene by treatment with butyllithium. When dissolved in tetrahydrofuran, it can be stored at -25 °C for hours, but decomposes rapidly at 0 °C. Copyright © 1996 Elsevier Science Ltd

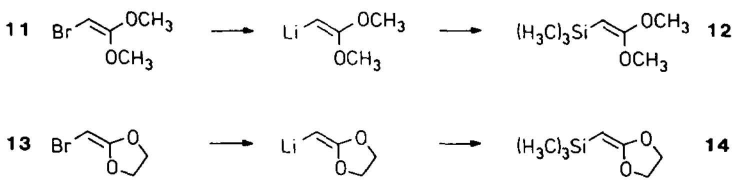
In the same way as 2-ethoxyvinyllithium [1, 2] can be conceived as a synthetical equivalent of the acetaldehyde derived enolate, 2,2-diethoxyvinyllithium **1** may be used as a masked ethyl acetate (ethoxycarbonylmethyl) anion. The organometallic reagent is instantaneously formed when butyllithium is added to an ethereal solution of 2-bromo-1,1-diethoxyethylene. Interception with electrophiles such as iodine or iodonium chloride, chlorotrimethylsilane, dimethyl sulfate, benzylbromide, butanal and pivalaldehyde gives the ketene acetals **2** (64%), **3** (31%), **4** (61%), **5** (64%), **6** (65% [after treatment of alcoholate with chlorotrimethylsilane : MO = LiO → $(H_3C)_3SiO$]) and **7** (67%). [3]



The ketene acetals may be immediately submitted to acid catalyzed hydrolysis to afford the corresponding ethyl esters. When aldehydes had been employed as the electrophiles, simultaneous dehydration of the intermediate β-hydroxy esters occurs producing α,β-unsaturated ester such as ethyl 4,4-dimethylpent-2-enoate (**8**, 65%), ethyl cinnamate (**9**, 94%) and ethyl *p*-chlorocinnamate (**10**, 78%).



In the same way as 2,2-diethoxyvinyllithium, 2,2-dimethoxyvinyllithium and 2,2-(1,3-dioxolan-2,2-ylidene)-vinyllithium have been generated from the corresponding bromides **11** [4] and **13** [4] by halogen/metal interconversion. Reaction with chlorotrimethylsilane at -75 °C afforded (2,2-dimethoxyvinyl)trimethylsilane (**12**, 67%) and [(2,2-dioxolan-2,2-ylidene)methyl]trimethylsilane (**14**, 72%), respectively.



Solutions of all these 2,2-dialkoxyvinyllithium reagents in tetrahydrofuran can be stored for hours at -25 °C. Thus,. their thermal stability equals or even surpasses that of (*Z*)-2-ethoxyvinyllithium [1] whereas the corresponding (*E*)-isomer was reported to decompose already at temperatures below -80 °C [1]. Comparing these structures, one is at first sight inclined to attribute a stabilizing, dipolar or coordinative effect to the alkoxy group occupying the *cis* position with respect to the metal. However, this conclusion might be fallacious since it does not take into account the differences in n-π conjugation energies [5] between ethoxyalkenes (enethers) and alkoxyacetylenes, the precursors and products of the elimination reactions under inspection. In other words, a more profound investigation deems warranted.

Typical working procedure : Precooled (-75 °C) tetrahydrofuran (40 mL) and 2-bromo-1,1-diethoxyethylene [6] (**1**; 3.7 mL, 4.9 g, 25 mmol) were consecutively added to butyllithium (25 mmol) from which the commercial solvent (hexane) had been stripped off. After 30 min at -75 °C, chlorotrimethylsilane (3.1 mL, 2.7 g, 25 mmol) was added. When the mixture had reached 25 °C, the solvent was evaporated and the residue distilled to afford (2,2-diethoxyvinyl)trimethylsilane as a colorless liquid; bp 59 - 60 °C/9 mmHg; n_D^{20} 1.4308; 64%.

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