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2-Ethoxyvinyllithiums and Diethoxyvinyllithiums : What Makes Them Stable or Fragile ?

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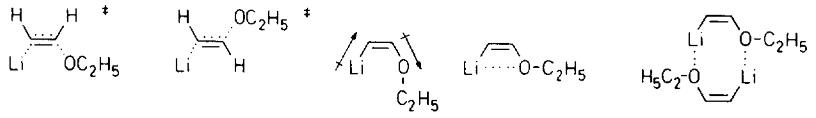
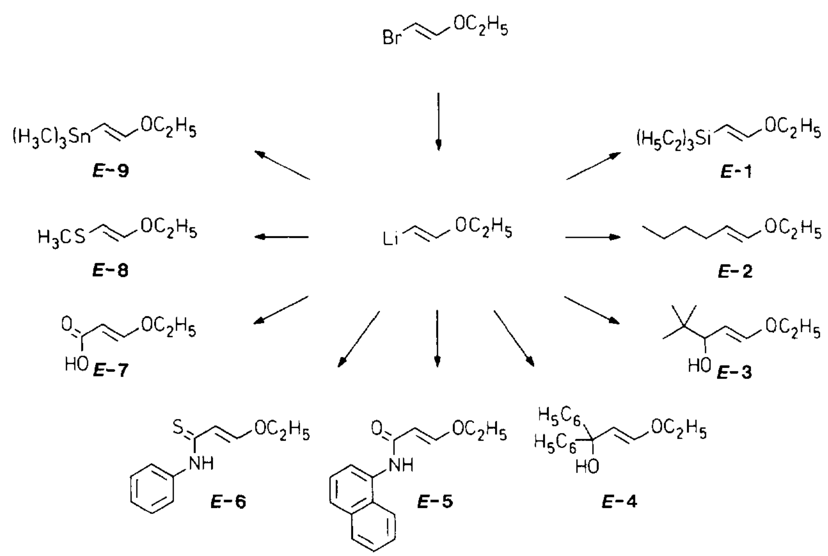
Abstract : The elusive (*E*)-2-ethoxyvinyllithium can be readily generated in tetrahydrofuran at -75 °C from (*E*)-1-bromo-2-ethoxyethylene by halogen/metal exchange and subsequently trapped with electrophiles. Alkylation opens a convenient entry to (*E*)-configurated enethers. (*E*)-2-Ethoxyvinyllithium decomposes rapidly at -50 °C whereas its (*Z*)-isomer, which lacks the possibility to eliminate lithium ethoxide in a favorable *anti*-periplanar process, is stable under the same conditions. (*E*)-1,2-Diethoxyvinyllithium even sustains reflux temperatures (approximately 75 °C). 2,2-Diethoxyvinyllithium and (*Z*)-1,2-diethoxyvinyllithium can be conserved at 0 °C although this time loss of alcoholate can occur in the *anti*-mode. Obviously it matters whether the energy-rich ethoxyacetylene is formed as the elimination product or simple acetylene, as in the case of (*E*)-2-ethoxyvinyllithium.

The (*Z*) and (*E*) isomers of 2-ethoxyvinyllithium were reported to decompose under loss of lithium ethoxide at temperatures above -30 °C and below -80 °C, respectively [1]. This striking difference in thermal stability may be rationalized in two ways. Either the (*E*) isomer is intrinsically weakened because of the well known preference of *anti*-periplanar over *syn*-periplanar elimination processes [2] or the (*Z*) isomer benefits from extra stabilization, whether a favorable combination of Li,C and C,O dipoles or an intramolecular, if not intra-aggregate, coordination of lithium to oxygen is at the origin.



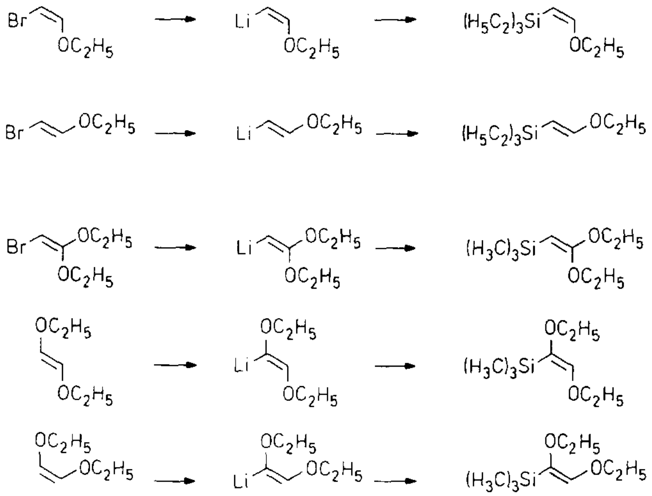
In order to clear up the alternative, we decided to study a series of alkoxyvinyllithium species in order to determine the threshold temperatures of their decomposition. The first task was to learn how to generate the elusive (*E*) isomer of 2-ethoxyvinyllithium under conditions where it could at least temporarily survive. The halogen/metal exchange accomplished between (*E*)-1-bromo-2-ethoxyethylene and butyllithium in neat tetrahydrofuran at -75 °C turned out to be the best method. When 15 min later chlorotriethylsilane was added, the silane ***E*-1** could be isolated in 57% yield. With butyl iodide, pivalaldehyde, benzophenone, 1-naphthylisocyanate, phenylisothiocyanate, carbon dioxide, dimethyl disulfide and chlorotrimethyltin the enether ***E*-2** (43%), the γ-hydroxyenethers ***E*-3** (64%) and ***E*-4** (75%), the carboxamide ***E*-5** (74%), the thiocarboxamide ***E*-6** (42%), the carboxylic acid ***E*-7** (75%), the enesulfide ***E*-8** (64%) and the organotin compound ***E*-9** (65%), all having the *trans* configuration, were obtained. Established methods leading to enethers either produce *cis*/*trans* mixtures [3] or the pure *cis* isomer [4] which is thermodynamically favored.



The choice of the solvent is crucial. Addition of other solvents such as hexane, diethyl ether or ethylene glycol dimethyl ether to the tetrahydrofuran medium gives inferior results. Nothing happens in 1 : 1 or 2 : 1 mixtures of diethyl ether and hexane during 1 h at -75 °C while mainly *hydrogen*/lithium exchange takes place at the halogen bearing site at higher temperatures (6 h at -50 °C or 16 h at -60 °C) [1].

To exploit the preparative potential of (*E*)-2-ethoxyvinyllithium, a better access to its precursor, the corresponding bromo compound, is highly desirable. So far, the 85 : 15 (*Z*/*E*) mixture collected after the dehydrobromination of 1,2-dibromoethyl ethyl ether had to be fractionated. A first improvement was achieved when the distillation was carried out under (*Z*/*E*) isomerizing conditions, the (*E*) isomer (bp 54 - 55 °C/50 mmHg) being more volatile than the (*Z*) isomer (bp 60 - 62 °C/50 mmHg). From a practical point of view, however, it is more convenient to start with an (*E*) enriched isomeric mixture and to destroy the (*Z*) isomer selectively by treatment with a solution of potassium *tert*-butoxide in boiling diethyl ether.

The practical problems being solved, we undertook the projected comparison of the thermal stability of ethoxyvinyllithiums. (*Z*)- and (*E*)-2-Ethoxyvinyllithium and 2,2-diethoxyvinyllithium [5] were generated by bromine/lithium interconversion with butyllithium, while (*Z*)- and (*E*)-1,2-diethoxyvinyllithium [6] were obtained from (*Z*)- and (*E*)-1,2-diethoxyethylene by hydrogen/metal interconversion with *tert*-butyllithium. Approximately 0.5 M solutions of the organolithium intermediates in tetrahydrofuran were immersed in cooling baths and kept 45 min at a given temperature before being trapped with chlorotrimethylsilane or chlorotriethylsilane. The interception products (*Z*)- and (*E*)-(2-ethoxyvinyl)triethylsilane (***Z*-1** and ***E*-1**), (2,2-diethoxyvinyl)trimethylsilane (**10**) and (*Z*)- and (*E*)-(1,2-diethoxyvinyl)trimethylsilane (***Z*-11** and ***E*-11**) were identified by gas chromatography using authentic samples for reference and the yields were determined by applying the technique of an internal standard.



Z-1

E-1

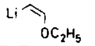
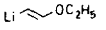
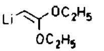
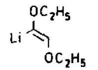
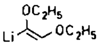
10

Z-11

E-11

The temperature was varied in 25 °C jumps. As soon as the range was identified where decomposition proceeded at a measurable rate, samples were withdrawn at fixed intervals. The yields of interception products were again determined by gas chromatography (Table).

Table . Yields of interception products obtained from solutions of (di)ethoxyvinyllithium compounds in tetrahydrofuran after trapping with chlorotriethylsilane or chlorotrimethylsilane as a function of the exposure time at threshold decomposition temperatures.

time					
	at -50°C	at -75°C	at 0°C	at +75°C	at 0°C
5 min	93%	90%	90%	88%	89%
15 min	92%	85%	30%	85%	86%
45 min	90%	86%	0%	40%	83%
2 h	89%	75%	-	25%	80%
6 h	86%	30%	-	-	-

The data reported above are meaningful only in a qualitative sense. The β-elimination of lithium ethoxide is not the only reaction mode that can account for the decomposition of the investigated organolithium intermediates. The latter may also be destroyed by air and moisture accidentally entering the vessel in the moment of sample withdrawal, by reaction with butylbromide formed as a by-product of the halogen/metal exchange or by proton abstraction from the solvent. Actually, the concentrations of 1-ethoxyvinyllithium [7] and (*E*)-1,2-diethoxyvinyllithium in boiling tetrahydrofuran (bath temperatures adjusted to 75 - 85 °C) decrease at approximately the same rate although the former reagent is unable to undergo a β-elimination process.

The contrasting temperature sensitivities of the organolithium species investigated cannot be rationalized on the basis of stabilizing oxygen-lithium interactions unless one makes quite arbitrary assumptions. The enhanced stability of 2,2-diethoxyvinyllithium and (*Z*)-1,2-diethoxyvinyllithium (both decomposing at 0 °C) relative to (*E*)-2-ethoxyvinyllithium (slow decomposition at -75 °C) would have to be attributed to coordination of lithium by oxygen atoms occupying the α- or *cis*-β-position, respectively. To allow for the still increased capacity of (*E*)-1,2-diethoxyvinyllithium to sustain thermal stress (decomposition around +75 °C), one would have to postulate that both effects can simultaneously operate without attenuation. We favor a more plausible explanation and impute the fragility of (*E*)-2-ethoxyvinyllithium, relative to its (*Z*) isomer, to the well-documented preference [2, 8] of *anti-* compared to *syn*-β-elimination. The protection provided by a second alkoxy group [9, 10], which retards thermal decomposition no matter whether located in the α- or β-position, then mainly reflects the differences in thermodynamic stability between an n,π-conjugated [11] vinyl ether and acetylene and, on the other hand, between a dialkoxyethylene and an energy-rich [11] alkoxy-acetylene. A qualitatively similar argument can be based on the differences in standard enthalpies of formation between ethane and ethyl methyl ether ($\Delta\Delta H_f°$ 31.5 kcal/mol), ethylene and methyl vinyl ether ($\Delta\Delta H_f°$ 38.1 kcal/mol) and acetylene and ethynyl methyl ether ($\Delta\Delta H_f°$ 31.3 kcal/mol) [12]. Of course, the inductive effect of the oxygen atom in the α-position also contributes to the stabilization of excess negative charge, although apparently only to a minor extent as judged from the proton affinity of the α-methoxyvinyl anion in the gas phase [13].

EXPERIMENTAL

1. Generalities

^{1}H-NMR spectra were recorded of samples dissolved in deuterochloroform at 400 MHz. For standard working practice and abbreviations, see recent articles [14] from this laboratory.

A series of previously unknown 2,2-diethoxyvinyl derivatives have been mentioned without details in a communication [5] related to the present topic. The preparation and the properties of these compounds are described in Section 3.

2. Generation and Interception of (*E*)-2-Ethoxyvinyllithium

(*E*)-1-Bromo-2-ethoxyethylene : A 65 : 35 (*Z/E*) mixture [1] of 1-bromo-2-ethoxyethylene (11 mL, 15 g, 0.10 mol) was added to potassium *tert*-butoxide (8.4 g, 75 mmol) in diethyl ether (0.15 L) and the suspension was heated to reflux for 2 h. Evaporation of the solvent followed by distillation afforded a colorless liquid; bp 60 - 62 °C/50 mmHg; d_4^{20} 1.41; n_D^{20} 1.4638; 22%. - The (*Z/E*) ratio was 1 : 99 according to gas chromatography (3 m, 5% SE-30, 70 °C; 5 m, 5% C-20M, 70 °C). - ^{1}H-NMR : δ 6.76 (1 H, d, *J* 12.0), 5.37 (1 H, d, *J* 12.0), 3.78 (2 H, q, *J* 7.0), 1.31 (3 H, t, *J* 7.0). - Analysis : calc. for C_4H_7BrO (151.00) C 31.82, H 4.67; found C 31.95, H 4.71%.

[(*E*)-2-Ethoxyvinyl]triethylsilane (*E*-1) : Precooled (-75 °C) tetrahydrofuran (50 mL) and (*E*)-1-bromo-2-ethoxyethylene (2.7 mL, 3.8 g, 25 mmol) were consecutively added to butyllithium (25 mmol) from which the commercial solvent (hexane) had before been stripped off. After 30 min at -75 °C, the mixture was treated with chlorotriethylsilane (4.2 mL, 3.8 g, 25 mmol). Evaporation of the solvent and distillation of the residue afforded product ***E*-1** [15]; bp 80 - 82 °C/9 mmHg; n_D^{20} 1.4486; 57%. - ^{1}H-NMR : δ 6.39 (1 H, d, *J* 15.2), 4.41 (1 H, d, *J* 15.2), 3.81 (2 H, q, *J* 7.0), 1.30 (3 H, t, *J* 7.0), 0.95 (9 H, t, *J* 7.8), 0.55 (6 H, q, *J* 7.8). - MS : 157 (33%, M^+ - 29), 131 (100%). - Analysis : calc. for $C_{10}H_{22}OSi$ (186.37) C 64.45, H 11.90; found C 64.84, H 11.89%.

(*E*)-1-Ethoxyhex-1-ene (*E*-2) : When proceeding exactly in the same way except for replacing chlorotriethylsilane by butyl iodide (2.9 mL, 4.6 g, 25 mmol) and adding hexamethylphosphoric triamide (13 mL, 13 g, 75 mmol), product ***E*-2** was formed. It was isolated by distillation and purified by preparative gas chromatography (6 m, 5% C-20M, 70 °C); bp 55 - 60 °C/60 mmHg; n_D^{20} 1.4183; 43%. - ^{1}H-NMR : δ 6.22 (1 H, d, *J* 12.8), 4.78 (1 H, dt, *J* 12.8, 7.4), 3.70 (2 H, q, *J* 7.0), 1.9 (2 H, m), 1.3 (4 H, m), 1.26 (3 H, t, *J* 7.0), 0.88 (3 H, t, *J* 7.4). - MS : 128 (55%, M^+), 85 (79%), 131 (100%). - Analysis : calc. for $C_8H_{16}O$ (128.22) C 74.94, H 12.58; found C 75.36, H 12.72%.

(*E*)-1-Ethoxy-3-hydroxy-4,4-dimethylpent-1-ene (*E*-3) : Using pivalaldehyde (2.7 mL, 2.2 g, 25 mmol) as the electrophile, gave a product mixture from which, after hydrolysis, the hydroxyenether ***E*-3** was extracted with diethyl ether and collected after distillation; bp 45 - 46 °C/0.3 mmHg; n_D^{20} 1.4462; 64%. - ^{1}H-NMR : δ 6.43 (1 H, d, *J* 12.5), 4.87 (1 H, dd, *J* 12.5, 9.0), 3.75 (2 H, dq, *J* 7.0, 1.0), 3.6 (1 H, m), 1.29 (3 H, t, *J* 7.0), 0.90 (9 H, s). - MS : 142 (37%), 141 (100%), 101 (62%). - Analysis : calc. for $C_9H_{18}O_2$ (158.24) C 68.31, H 11.47, found C 68.37, H 11.47%.

(*E*)-3-Ethoxy-1,1-diphenylprop-2-ene-1-ol (*E*-4) : Reaction with benzophenone (4.6 g, 25 mmol) gave the γ-hydroxyenether ***E*-4** after hydrolysis, extraction with diethyl ether and chromatography on silica gel (using a 1 : 2 mixture of ethyl acetate and hexane as the eluent); mp 67 - 68 °C (crystallized from ethyl acetate); 75%. - ^{1}H-NMR : δ 7.3 (10 H, m), 6.23 (1 H, d, *J* 12.6), 5.50 (1 H, d, *J* 12.6), 3.78 (2 H, q, *J* 7.0), 1.28 (3 H, t, *J* 7.0). - MS : 208 (77%, M^+ - C_2H_6O), 207 (90%), 105 (100%). - Analysis : calc. for $C_{17}H_{18}O_2$ (254.33) C 80.28, H 7.13; found C 80.47, H 7.08%.

***N*-[(*E*)-3-Ethoxyprop-2-enoyl]-1-naphthamide (*E*-5)** : With 1-naphthylisocyanate (4.2 g, 3.6 mL, 25 mmol) the amide ***E*-5** was obtained. Hydrolysis, extraction with diethyl ether, chromatography on silica gel using a 1 : 2 (v/v) mixture of ethyl acetate and hexane as the eluent gave colorless prisms; mp 132 - 134 °C (from benzene); 74%. - ^{1}H-NMR : (D_3CCOCD_3) : δ 8.1 (1 H, m), 8.0 (1 H, m), 7.9 (1 H, m), 7.69 (1 H, d, *J* 8.3), 7.60 (1 H, d, *J* 12.3), 7.5 (3 H, m), 5.86 (1 H, d, *J* 12.3), 4.00 (2 H, q, *J* 7.0), 2.85 (1 H, s), 1.32 (3 H, t, *J* 7.0). - MS : 242 (23%, M^+ + 1), 241 (33%, M^+), 143 (100%). - Analysis : calc. for $C_{15}H_{15}NO_2$ (241.29) C 74.67, H 6.27; found C 74.66, C 5.93%.

***N*-[(*E*)-3-Ethoxyprop-2-enoyl]thiobenzamide (*E*-6)** : With phenylisothiocyanate (3.0 mL, 3.4 g, 25 mmol) the thioamide ***E*-6** was formed. Hydrolysis, extraction with diethyl ether, chromatography on silica gel using a 1 : 4 (v/v) mixture of ethyl acetate and hexane gave colorless needles; mp 108 - 109 °C (from ethyl acetate); 42%. - ^{1}H-NMR : δ 8.10 (1 H, d, *J* 11.5), 7.3 (5 H, m), 5.94 (1 H, dd, *J* 11.5, 1.5), 4.01 (2 H, q, *J* 7.0), 1.58 (1 H, s), 1.32 (3 H, t, *J* 7.0). - MS : 208 (27%, M^+ + 1), 207 (48%), 87 (100%). - Analysis : calc. for $C_{11}H_{13}NOS$ (207.30) C 63.74, H 6.33; found C 63.96, H 6.09%.

(*E*)-3-Ethoxypropenoic acid [16] **(*E*-7)** : When the reaction mixture containing the organometallic intermediate was poured on dry-ice, the acid ***E*-7** was isolated after extraction into alkaline aqueous medium, acidification, extraction with diethyl ether and crystallization (from water); mp 109 - 111 °C; 75%. - ^{1}H-NMR : δ 7.68 (1 H, d, *J* 12.5), 5.17 (1 H, d, *J* 12.5), 3.95 (2 H, q, *J* 7.1), 1.36 (3 H, t, *J* 7.1). - MS : 117 (38%, M^+ + 1), 116 (70%, M^+), 70 (100%).

(*E*)-1-Ethoxy-2-(methylthio)ethylene (*E*-8) : Treatment with dimethyl disulfide (2.3 mL, 2.4 g, 15 mmol) and immediate distillation afforded a colorless liquid; bp 63 - 65 °C/20 mmHg (lit. [17] bp : not specified); n_D^{20} 1.4751; 64%. - ^{1}H-NMR : δ 6.70 (1 H, d, *J* 12.2), 5.35 (1 H, d, *J* 12.2), 3.80 (2 H, q, *J* 7.0), 2.16 (3 H, s), 1.29 (3 H, t, *J* 7.0). - MS : 119 (30%, M^+ + 1), 118 (100%, M^+), 105 (56%). - Analysis : calc. for $C_5H_{10}OS$ (118.20) C 50.81, H 8.53; found C 50.72, H 8.42%.

[(*E*)-2-Ethoxyvinyl]trimethyltin (*E*-9) : When chlorotrimethyltin (6.3 mL, 5.0 g, 25 mmol) was added to the solution containing the organometallic intermediate and the mixture was immediately distilled, the stannane ***E*-9** was collected as a colorless liquid; bp 48 - 49 °C/5 mmHg; n_D^{20} 1.4908; 65%. - ^{1}H-NMR : δ 6.24 (1 H, d, *J* 15.5), 4.71 (1 H, d, *J* 15.5), 3.79 (2 H, q, *J* 7.1), 1.28 (3 H, t, *J* 7.1), 0.12 (9 H, s). - Analysis : the compound was not stable enough to be mailed to an outside laboratory.

3. Generation and Interception of 2,2-Diethoxyvinyllithium

(2,2-Diethoxyvinyl)trimethylsilane [5] **(10)** : Precooled (-75 °C) tetrahydrofuran (40 mL) and 2-bromo-1,1-diethoxyethylene [18] (3.5 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 (3.2 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 silane **10** as a colorless liquid; bp 59 - 60 °C/9 mmHg; n_D^{20} 1.4308; 64%. - ^{1}H-NMR : δ

3.95 (2 H, q, J 6.9), 3.80 (2 H, q, J 6.9), 3.0 (1 H, s), 1.30 (3 H, t, J 6.9), 1.24 (3 H, t, J 6.9), 0.07 (9 H, s). - MS 76% (M^+ + 1), 161 (100%). - Analysis : calc. for $C_9H_{20}SiO_2$ (188.34) C 57.39, H 10.70; found C 57.32, H 10.65%.

1,1-Diethoxy-2-iodoethylene [5] : Treatment with iodonium chloride (4.1 g, 25 mmol) rather than with chlorotrimethylsilane afforded a viscous, colorless liquid, bp 30 - 35 °C/0.3 mmHg; 31%. - ^{1}H-NMR : δ 4.04 (2 H, t, J 7.1), 3.87 (2 H, q, J 7.1), 3.85 (1 H, s), 1.34 (3 H, t, J 7.1), 1.30 (3 H, t, J 7.1). - Analysis : calc. for $C_6H_{11}IO_2$ (242.05) C 29.77, H 4.58; found C 29.83, H 4.82%.

1,1-Diethoxyprop-1-ene [5, 19] : Treatment with dimethyl sulfate (2.4 mL, 3.2 g, 25 mmol) and subsequent distillation give a colorless liquid; bp 53 - 54 °C/65 mmHg; n_D^{20} 1.4150; 61%. - ^{1}H-NMR : δ 3.92 (2 H, q, J 7.0), 3.73 (2 H, q, J 7.0), 3.70 (1 H, q, J 6.3), 1.57 (3 H, d, 6.3), 1.30 (3 H, t, J 7.0), 1.28 (3 H, t, J 7.0). - Analysis : calc. for $C_7H_{14}O_2$ (130.19) C 64.58, H 10.84; found C 64.40, H 10.95%.

1,1-Diethoxy-3-phenylprop-1-ene [5, 20] : In the same way, a reaction with benzyl bromide (3.0 mL, 4.3 g, 25 mmol) was performed to obtain the product again in form of a colorless liquid; bp 70 - 72 °C/0.3 mmHg; n_D^{20} 1.5070. - ^{1}H-NMR : δ 7.2 (5 H, m), 3.98 (2 H, q, J 7.1), 3.87 (1 H, t, J 7.3), 3.79 (2 H, q, J 7.1), 3.41 (2 H, d, J 7.3), 1.33 (3 H, t, J 7.1), 1.29 (3 H, t, J 7.1). - Analysis : calc. for $C_{13}H_{18}O_2$ (206.29) C 75.69, H 8.80; found C 75.56, H 8.70%.

[(3,3-Ethoxy-1-propylprop-2-enyl)oxy]trimethylsilane [5] : Interception with butanal (2.3 mL, 1.8 g, 25 mmol) at -75 °C followed by the addition of chlorotrimethylsilane (3.2 mL, 2.7 g, 25 mmol) at 0 °C and direct distillation afforded a colorless liquid; mp 64 - 65 °C/1 mmHg; n_D^{20} 1.4298; 65%. - ^{1}H-NMR : δ 4.49 (1 H, dt, J 8.9, 6.5), 3.9 (2 H, m), 3.75 (2 H, dq, J 7.0, 1.5), 3.66 (1 H, d, J 8.9), 1.4 (5 H, m), 1.30 (3 H, t, J 7.0), 0.90 (3 H, t, J 7.3), 0.11 (9 H, s). - MS : 262 (20%, M^+ + 2), 261 (43%, M^+ + 1), 73 (100%). - Analysis : calc. for $C_{13}H_{28}O_3Si$ (260.45) C 59.95, H 10.84; found C 59.95, H 10.70%.

1,1-Diethoxy-4,4-dimethylpent-1-en-3-ol [5] : Treatment of the reaction mixture containing the organolithium intermediate at -75 °C with pivalaldehyde (2.7 mL, 2.2 g, 25 mmol), hydrolysis, extraction with diethyl ether and distillation gave a colorless oil; bp 59 - 60 °C/1 mmHg; n_D^{20} 1.4451; 64%. - ^{1}H-NMR : δ 4.17 (1 H, dd, J 8.8, 3.6), 4.0 (2 H, m), 3.8 (2 H, m), 3.76 (1 H, d, J 8.8), 3.60 (1 H, d, J 3.6), 1.32 (3 H, t, J 7.0), 1.25 (3 H, t, J 7.1), 0.91 (9 H, s). - MS : 203 (100%, M^+ + 1), 202 (1%, M^+), 186 (29%); 185 (95%). - Analysis : calc. for $C_{11}H_{22}O_3$ (202.29) C 65.31, H 10.96; found C 65.22, H 10.79%.

Vigorous stirring with 10% hydrochloric acid (10 mL) for 30 min at 25 °C converted the ketene acetal into **ethyl 4,4-dimethylpent-2-enoate** [21] which was isolated by extraction with diethyl ether (2 × 25 mL), washing of the combined organic layers with a saturated aqueous solution of sodium hydrogen carbonate (2 × 25 mL) and brine (25 mL), drying, evaporation, chromatography (elution from silica gel with a 1 : 10 mixture of ethyl acetate and hexane) and distillation; bp 105 - 106 °C/3 mmHg; n_D^{20} 1.5588; 71%. - ^{1}H-NMR : δ 6.95 (1 H, d, J 16.0), 5.73 (1 H, d, J 16.0), 4.18 (2 H, q, J 7.2), 1.31 (3 H, t, J 7.2), 1.10 (9 H, s).

(2,2-Dimethoxyvinyl)trimethylsilane [5] : Prepared, as described for silane **10** (see above), from 2-bromo-1,1-dimethoxyethylene [21] (2.8 mL, 4.2 g, 25 mmol), butyllithium (25 mmol) and chlorotrimethylsilane (3.2 mL, 2.7 g, 25 mmol); bp 68 - 70 °C/45 mmHg; n_D^{20} 1.4318; 67%. - ^{1}H-NMR : δ 3.69 (3 H, s), 3.67 (3 H, s), 3.03 (1 H, s), 0.07 (9 H, s). - MS : 161 (100%, M^+ + 1), 160 (1%, M^+), 106 (34%). - Analysis : calc. for $C_7H_{16}O_2Si$ (160.29) C 52.45, H 10.06; found C 52.51, H 10.12%.

1,1-Dimethoxy-3-phenylprop-1-ene : Upon reaction with benzyl bromide (3.0 mL, 4.3 g, 25 mmol) at -75 °C followed by immediate distillation, a colorless oil was obtained; bp 60 - 63 °C/1 mmHg; n_D^{20} 1.5282; 56%. - ^{1}H-NMR : δ 7.3 (5 H, m), 3.78 (1 H, t, J 7.3), 3.66 (3 H, s), 3.58 (3 H, s), 3.38 (2 H, d, J 7.3). - Analysis : calc. for $C_{11}H_{14}O_2$ (178.23) C 74.13, H 7,92; found C 73.77, H 7.52%.

[2,2-(1,3-Dioxolan-2,2-ylidene)vinyl]trimethylsilane : Prepared, as described for silane **10** (see above), from 2-bromomethylene-1,3-dioxolane [22] (2.8 mL, 4.1 g, 25 mmol), butyllithium (25 mmol) and chlorotrimethylsilane (3.2 mL, 2.7 g, 25 mmol); bp 69 - 70 °C/12 mmHg; n_D^{20} 1.4602; 72%. - ^{1}H-NMR : δ 4.2 (4 H, m), 3.29 (1 H, s), 0.09 (9 H, s). - Analysis : calc. for $C_7H_{14}SiO_2$ (158.27) C 53.12, H 8.92; found C 53.14, H 8.89%.

4. Generation and Interception of 1,2-Dialkoxyvinyllithiums

Careful fractionation of the (*Z/E*) mixture of 1,2-diethoxyethylene [22] using a Fischer "Spaltrohr" column permitted the isolation of pure isomers.

(*E*)-1,2-Diethoxyethylene : bp 58 - 60 °C/45 mmHg; d_4^{20} 0.88; n_D^{20} 1.4140. - ^{1}H-NMR : δ 6.27 (2 H, s), 3.64 (4 H, q, *J* 7.1), 1.25 (6 H, t, *J* 7.1). - Analysis : calc. for $C_6H_{12}O_2$ (116.04) C 62.04, H 10.41; found C 61.96, H 10.41%.

(*Z*)-1,2-Diethoxyethylene : bp 61 - 63 °C/45 mmHg; d_4^{20} 0.89; n_D^{20} 1.4256. - ^{1}H-NMR : δ 5.32 (2 H, s), 3.89 (4 H, q, *J* 7.1), 1.29 (6 H, t, *J* 7.1). - Analysis : calc. for $C_6H_{12}O_2$ (116.04) C 62.04, H 10.41; found C 61.84, H 10.40%.

[(*Z*)-1,2-Diethoxyvinyl]trimethylsilane (*Z*-11) : A precooled (-75 °C) solution of (*E*)-1,2-diethoxyethylene (3.3 mL, 2.9 g, 25 mmol) in tetrahydrofuran (60 mL) was added to *tert*-butyllithium (25 mmol) from which the commercial solvent (pentane) had beforehand been stripped off. After 3 h at -25 °C, chlorotrimethylsilane (3.2 mL, 2.7 g, 25 mmol) was added. After removal of the solvent, the residue was distilled under reduced pressure and a colorless liquid was collected; bp 73 - 74 °C/18 mmHg; n_D^{20} 1.4320; 75%. - ^{1}H-NMR : δ 6.41 (1 H, s), 3.63 (2 H, q, *J* 7.1), 3.55 (2 H, q, *J* 7.0), 1.24 (3 H, t, *J* 7.0), 1.22 (3 H, t, *J* 7.1), 0.15 (9 H, s). - MS : 188 (5%, M^+), 149 (11%), 83 (100%). - Analysis : calc. for $C_9H_{20}O_2Si$ (188.34) C 57.39, H 10.70; found C 57.15, H 10.86%.

[(*E*)-1,2-Diethoxyvinyl]trimethylsilane (*E*-11) : Prepared in the same way as its isomer ***Z*-11**; bp 81 - 82 °C/18 mmHg; n_D^{20} 1.4340. - ^{1}H-NMR : δ 5.47 (1 H, s), 3.89 (2 H, q, *J* 7.0), 3.82 (2 H, q, *J* 7.0), 1.29 (3 H, t, *J* 7.0), 1.24 (3 H, t, *J* 7.0), 0.11 (9 H, s). - MS : 188 (4%), 149 (16%), 83 (100%). - Analysis : calc. for $C_9H_{20}O_2Si$ (188.34) C 57.39, H 10.70; found C 57.47, H 10.73%.

5. Thermal Stability of (Di)Ethoxyvinyllithiums as a Function of the Temperature

a) *Solvent Effects on the Storability*

Threshold decomposition temperatures in tetrahydrofuran can be taken or extrapolated from the data compiled in the Table (see above). At -50 °C, (Z)-*2-ethoxyvinyllithium* can be almost indefinitely conserved not only in tetrahydrofuran, but also in diethyl ether (although the halogen/metal exchange is complete only after several hours in this solvent) and (mono)ethyleneglycol dimethyl ether (MEGME), but it survives, even for a short while, at -25 °C only in the latter solvent (60% after 5 min). Whereas (E)-*2-ethoxyvinyllithium* is reasonably stable in tetrahydrofuran (THF) at -75 °C and some remainders can still be trapped in this solvent even at -50 °C (11% after 5 min, 0% after 15 min), it instantaneously decomposes in MEGME at -75 °C and in diethyl ether at -75 °C or even -100 °C. On the other hand, 2,2-diethoxyvinyllithium is most stable in diethyl ether (DEE) at 0 °C (after 15 min 90%, 30% and 0% in DEE, THF and MEGME, respectively) while at -25 °C no differences are apparent. (E)-*1,2-Diethoxyvinyllithium* is perfectly stable in any ethereal solvent at +50 °C. However, (Z)-*1,2-diethoxyvinyllithium* decomposes at 0 °C more slowly in DEE (88% and 80% after 0.5 and 2 h, respectively) than in THF (61% and 0% after 0.5 and 2 h).

b) *Characterization of (Z)-2-Ethoxyvinyllithium*

[(*Z*)-2-Ethoxyvinyl]triethylsilane (*Z*-1) : At -75 °C, (*Z*)-1-bromo-2-ethoxyethylene (2.7 mL, 3.8 g, 25 mmol) and, 30 min later, chlorotriethylsilane (4.2 mL, 3.8 g, 25 mmol) were added to a solution of butyllithium (25 mmol) in tetrahydrofuran (35 mL) and hexane (15 mL). Immediate distillation afforded gas chromatographically pure silane *Z*-**1** [15]; bp 74 - 75 °C/8 mmHg; n_D^{20} 1.4460; 72%. - ^{1}H-NMR : δ 6.63 (1 H, d, *J* 8.5), 4.10 (1 H, d, *J* 8.5), 3.87 (2 H, q, *J* 7.0), 1.22 (3 H, t, *J* 7.0), 0.93 (9 H, t, *J* 7.9), 0.59 (6 H, q, *J* 7.9). - MS : 189 (4%, M^+ + 1), 188 (15%, M^+), 131 (100%. - Analysis : calc. for $C_{10}H_{22}OSi$ (186.37) C 64.45, H 11.90; found C 64.81, H 11.95%.

c) *Decomposition Products*

The acetylene which is set free from (*Z*)- and (*E*)-2-ethoxyvinyllithium by β-elimination of lithium ethoxide is immediately converted into lithium acetylide and dilithioacetylene under the reaction conditions. The latter intermediates have been identified as their adducts to pivalaldehyde, 4,4-dimethylpent-1-yn-3-ol [23] and 2,2,7,7-tetramethyloct-4-yne-3,6-diol [24] (*meso*/*dl* mixture, one component crystallizing from diethyl ether, mp 110 - 111 °C). Trapping of the ethoxyethynyllithium generated upon lithium ethoxide elimination from any of the diethoxyvinyllithium species with chlorotriethylsilane afforded ethoxytriethylsilane [25] and (ethoxyethynyl)-triethylsilane [26].

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