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Reactivity of dichlorosilanes with lithium ester enolates: synthesis of 3,3-disubstituted 3-silaglutarates

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Abstract

3,3-Disubstituted 3-silaglutarates were synthesized by reaction of the lithium enolate of ethyl acetate with dichlorosilanes at −94°C. When a phenyl group is linked to the silicon atom the reaction in THF gave mainly the silaglutarate. In other cases alkylsilylketene acetals were formed in proportions similar to or greater than that of the silaglutarate. The presence of HMPA increased the ratio of *C*- to *O*-silylated products and allowed the preparation of 3,3-dialkyl 3-silaglutarates in good yield.

Keywords: 3-silaglutarates; Dichlorosilanes; Lithium enolates

1. Introduction

We recently described the preparation of optically-active silicon centred chiral compounds by the lipase-catalyzed transesterification of isobutyric esters with 2-sila-1,3-propanediols [1]. In the course of our research on substrates for enzymatic reactions we have focussed on 3-substituted 3-silaglutarates since many reports have been devoted to the synthesis of optically active compounds by lipase- or esterase-catalyzed hydrolysis of 3-substituted glutarates [2–4]. However, to avoid any substitution at the silicon atom [5] during the enzymatic hydrolysis of 3-monosubstituted 3-silaglutarates, we decided to synthesize only 3,3-disubstituted compounds.

To our knowledge, the synthesis of 3-silaglutarates has been reported once only, and this patented method involves the reaction of bis(trifluoromethylsulfonyloxy) silanes with esters [6]. To avoid the preparation of bis(sulfonyloxy)silanes we have investigated another approach to silaglutarates, by analogy with the syntheses of α-silylesters. 2-Silylated esters have usually been synthesized by condensation of the Grignard reagent of a (chloromethyl)silane with an alkyl chloroformate [7], by insertion of a diazoacetate into a Si–H bond [8], or by reaction of an halosilane with an ester enolate or an α-metallated ester [9,10]. Mercury [9a,11], tin [9b,11], zinc [9c,12], magnesium [9d], and sodium ester derivatives [9e,9f,13] have been employed for the preparation of α-silylesters, but lithium enolates [10] have been used more frequently. However competitive formation of alkylsilylketene acetals was often observed.

The reaction of trimethylchlorosilane with the lithium enolate of methyl, ethyl or trimethylsilyl acetates or with the dianion of acetic acid in THF gave equimolecular mixtures of an α-silylated ester and a silylketene acetal [10a,10c,14]. The ratio of *C*- to *O*-silylated products was increased by the use of *t*-butyl ester [10c], by addition of HMPA as cosolvent [10c,15], and, in the case of trimethylsilyl acetate, by allowing the lithium derivative to stand for a long time at −70°C before the addition of the chlorosilane [16]. Reversely, the use of phenyl acetate led to the silylketene acetal [17]. In some cases heating or Lewis-acid catalysis allowed the isomerization of silylketene acetals to α-silylesters [9a,9b,18]. The reaction of acetate lithium enolates with diphenylmethylchlorosilane in THF gave only the α-silylated ester [19].

Due to the commercial availability of various dichlorosilanes we investigated their reactivity with acetate lithium enolates, despite the reported unsuccessful attempt to prepare a silaglutarate by reaction of an

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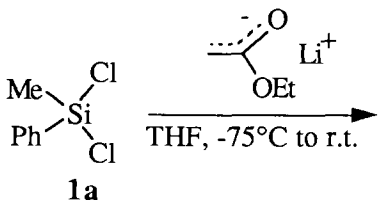
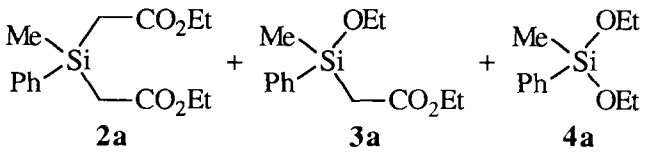


1a



2a 3a 4a

enolate/1a	Proportions of 2a	3a	4a
2/1	78	15	7
3/1	58	28	14
4/1	36	9	55

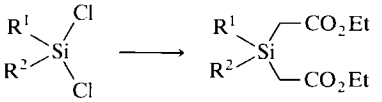
α-bromoacetate with zinc in the presence of a dichlorosilane [9c].

2. Results and discussion

Addition of dichloromethylphenylsilane (**1a**) to a solution of the lithium enolate of ethyl acetate (Li enolate/**1a** = 2/1) in a mixture of THF-hexane maintained between −75 and −70°C followed by warming to room temperature and aqueous work-up gave mainly diethyl 3-methyl-3-phenyl-3-silaglutarate (**2a**), ethyl (ethoxymethylphenylsilyl)acetate (**3a**) and diethoxymethylphenylsilane (**4a**). The isolated yield of silaglutarate **2a** was about 62% and some high molecular weight compounds were also observed.

When the ratio of lithiated ethyl acetate to **1a** was higher than in the stoichiometry shown, the proportion of ethoxysilanes **3a** + **4a** increased (see above). Under stoichiometric conditions, a higher proportion of the silaglutarate (**2a**/**3a**/**4a** = 85/9/6) and a better yield of the isolated product occurred when the reaction was run between −95 and −90°C followed by quenching at −30°C. With these conditions different dichlorosilanes were treated with lithiated ethyl acetate in THF. The yields of pure silaglutarates **2a–g** isolated by silica gel column chromatography are reported in Table 1, a small amount of an ethyl (ethoxysilyl)acetate (**3**) generally being eluted before the silaglutarate. The yields of silaglutarate were good with the dichlorophenylsilanes **1a** and **1f** but only poor with the other dichlorosilanes **1b–e** and **1g**. In these cases, the ^{1}H NMR spectra of the crude reaction mixtures after evaporation of the solvents showed the presence of silylketeneacetals.

Table 1
Yield of diethyl 3-silaglutarates isolated after reaction of lithium enolate of ethyl acetate with dichlorosilanes (%)



1 2

	R^1	R^2	in THF	in THF+HMPA
a	methyl	phenyl	73	64
b	methyl	octyl	26	74
c	methyl	vinyl	44	65
d	methyl	2-(4-methylphenyl)ethyl	15	68
e	methyl	2-exo-bicyclo[2.2.1]heptyl	< 5 *	61
f	allyl	phenyl	84	**
g	$-(CH_2)_4-$		~ 5 *	39

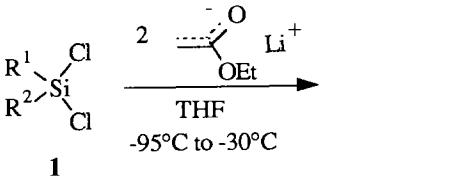
* Estimated by ^{1}H NMR spectroscopy. Bis(vinyloxy)silane (**6**) was the main product.
** Not attempted.

Mixtures of a silaglutarate **2**, an ethyl (1-ethoxyvinyloxy)silylacetate (**5**) and a bis(1-ethoxyvinyloxy) silane (**6**) [20] were generally obtained. In the case of the 2-bicyclo[2.2.1]heptylmethylsilane (**1e**) and the silacyclopentane (**1g**), the bis(1-ethoxyvinyloxy)silanes **6e** and **6g** were the main products of the reaction and could easily be isolated by distillation.

Moreover the presence of HMPA in the reaction mixture (4 moles for each lithium atom) appeared to be beneficial and allowed the synthesis of the expected silaglutarates **2** with satisfactory yields (see Table 1) after aqueous work-up and purification.

Attempts to isomerize the silylketeneacetals **5b** and **6b** to silaglutarate **2b** by reaction with mercuric iodide [9a] or trimethylaluminium [18] were unsuccessful.

The divinyloxysilacyclopentane (**6b**) reacts with benzaldehyde at room temperature without a catalyst to give the diethyl 4,6-dioxa-3,7-diphenyl-5-silanonanedioate (**7**). This confirms the recently reported enhanced reactivity of monovinyloxysilacycloalkanes [21].



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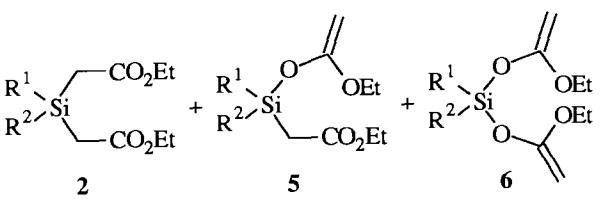
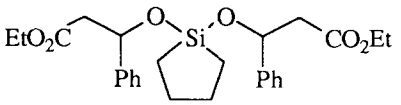


2 5 6

R^1 and R^2 ≠ Ph



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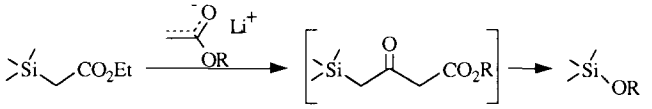
When the reaction of lithiated ethyl acetate with the dichlorosilane **1a** was performed in THF without HMPA the main by-products were ethoxysilanes **3a** and **4a** (vide supra). Alkoxysilanes were also noticed after the reaction of an α-bromoester with zinc in the presence of a chlorosilane [9c]. The enhancement of the amount of alkoxysilanes when the ratio of ethyl acetate enolate to **1a** was increased suggests that the formation of alkoxysilanes may result, in part, from the degradation of a γ-silyl β-ketoester enolate obtained after Claisen condensation of an α-silylated ester with a metallated alkyl acetate.



An attempt to prepare a γ-silyl β-ketoester by reaction of the dianion of ethyl acetoacetate with chlorodimethylthexylsilane yielded ethoxydimethylthexylsilane and the reaction of the lithium enolate of methyl acetate with the diethyl silaglutarate **2a** in THF gave dimethoxymethylphenylsilane. Treatment, under the same conditions, of the silaglutarate **2a** with lithium methoxide (which could result from the decomposition of lithiated methyl acetate with formation of ketene) gave a much lower yield of dimethoxysilane.

Various attempts to hydrolyze **2a–d** at pH = 7.2 in the presence of an esterase (from porcine liver [PLE] or horse liver) or a lipase (from pig pancreas or *Candida rugosa* or *Chromobacterium viscosum*) were unsuccessful. Generally no hydrolysis occurred. In some cases a very slow addition of base to the reaction mixture was necessary to maintain the pH at 7.2 but no hemiester could be isolated. One reason of the low reactivity of the silaglutarates with the enzymes tested is probably a steric problem due to the presence of the two substituents on the silicon atom. This hypothesis was supported by the fact that the initial reaction rate of PLE-catalyzed hydrolysis of diethyl 3,3-dimethylglutarate was at least 400 times slower than the initial rate of hydrolysis of the unsubstituted diethyl glutarate under the same conditions.

This work shows that it is possible to prepare 3-silaglutarates by reaction of dichlorosilanes with the lithium enolate of ethyl acetate. Concerning the problem of competitive *O*- and *C*-silylation, similar results to those reported in the case of monochlorosilanes were observed. In THF, *C*-silylated esters are the major product, or the sole product, when the silicon atom bears a phenyl group. Without a phenyl group on the silicon a mixture of silaglutarate and alkylsilylketeneacetal was obtained and the ratio of *C*- to *O*-silylated products can be increased by the presence of HMPA.

3. Experimental section

NMR spectra were recorded on Bruker AM 200 or AM 250 spectrometers. Mass spectra were determined at an ionizing voltage of 70 eV. Column chromatography was performed with silica gel (70–230 Mesh). TLC was performed on 0.25 mm silica gel (Merck 60 F_{254}). Dry solvents were obtained as follows: THF was distilled over sodium-benzophenone and HMPA was distilled over CaH_2 under reduce pressure. Dichlorosilanes **1a–1g** were purchased from Petrach Systems Inc. and were distilled before use.

General procedure for the reaction in THF: A 1.6 M solution of Li^{n}Bu in hexane (4.7 ml, 7.5 mmol) was added to a stirred solution of diisopropylamine (1.15 ml, 8.2 mmol) in THF (10 ml) at 0°C placed in a two-necked round-bottom flask equipped with a thermometer and maintained under argon. Stirring was continued for 15 min, the solution of LDA was cooled to −75°C and ethyl acetate (0.75 ml, 7.7 mmol) was added at such a rate as to maintain the temperature between −75 and −70°C. After 15 min at −75°C the reaction mixture was cooled at −95°C (hexane + liquid N_2) and the dichlorosilane (3.75 mmol) was dropped in at such a rate as to maintain the temperature between −95 and −90°C. After the addition, the temperature was allowed to reach −30°C (~ 1.5 h) and then an aqueous solution of $NaHCO_3$ (20 ml) and diethyl ether (50 ml) was added. The organic phase was separated, washed with water (3 × 10 ml), dried over Na_2SO_4 and the solvents were removed in vacuo. The silaglutarate was purified by silica-gel column chromatography and, in some cases, by bulb-to-bulb distillation under reduced pressure.

General procedure for the reaction in THF + HMPA: The same procedure was used, but after the preparation of the lithium enolate of ethyl acetate, HMPA (5.2 ml) was added to the reaction mixture at such a rate as to maintain the temperature between −70 and −75°C. Then the reaction mixture was cooled to −95°C and the experiment proceeded as described above.

3.1. Diethyl 3-methyl-3-phenyl-3-silaglutarate (2a)

R_f = 0.28 (hexane/Et_2O: 3/1). Bp: 160–170°C/0.05 mmHg. IR (neat) (cm^{-1}): 3040; 2980; 1730 ($\nu_{C=O}$); 1400; 1250 (ν_{Si-C}); 1100; 1040; 870; 810 (ν_{Si-C}); 730; 700. ^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm): 7.65–7.55 (m, 2H); 7.52–7.35 (m, 3H); 4.05 (q, J = 7.2 Hz, 4H); 2.25 (s, 4H); 1.15 (t, J = 7.2 Hz, 6H); 0.55 (s, 3H). ^{13}C NMR ($CDCl_3$, 50,3 MHz) δ (ppm): −4.46 (SiCH_3); 14.13 (O–CH_2–CH_3); 24.51 (Si–CH_2–C=O); 60.14 (O–CH_2–CH_3); 127.90; 130.01; 133.22; 133.71; 171.62 (C=O). ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ (ppm): −3.63.

MS (M = 294) *m/z* (%): 269 (12, $M^+ - 15$); 225(18); 224(18); 223(100); 167(13); 165(11); 139(18); 137(12); 121(15); 105(18); 91(22); 77(15). Anal. calcd. for $C_{15}H_{22}O_4Si$: C, 61.20; H, 7.54. Found: C, 61.36; H, 7.63%.

3.2. Ethyl (ethoxymethylphenylsilyl)acetate (3a)

R_f = 0.62 (hexane/Et_2O: 3/1). IR (neat) (cm^{-1}): 2960; 1730 ($\nu_{C=O}$); 2430; 1250 (ν_{Si-C}); 1090; 1030; 810 (ν_{Si-C}); 780; 730; 690. ^1H NMR ($CDCl_3$, 200 MHz) δ (ppm): 7.65–7.55 (m, 2H); 7.52–7.35 (m, 3H); 4.05 (q, J = 7.2 Hz, 2H); 3.75 (q, J = 7.2 Hz, 2H); 2.25 (s, 2H); 1.2 (t, J = 7.2 Hz, 3H); 1.10 (t, J = 7.2 Hz, 3H); 0.24 (s, 3H). ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ (ppm): −0.11. MS (M = 252) *m/z* (%): 224(17); 223(100, $M^+ - 29$); 165 (11, $M^+ - 87$); 160(38); 139(16); 137(13); 121(16); 91(16); 77(18).

3.3. Diethoxmethylphenylsilane (4a)

R_f = 0.80 (hexane/Et_2O: 3/1). IR (neat) (cm^{-1}): 2980; 2880; 1430; 1250 (ν_{Si-C}); 1100; 1090; 950; 800 (ν_{Si-C}); 780; 730. ^1H NMR ($CDCl_3$, 200 MHz) δ (ppm): 7.85–7.70 (m, 2H); 7.35–7.24 (m, 3H); 3.70 (q, J = 7.1 Hz, 4H); 1.15 (t, J = 7.1 Hz, 6H); 0.35 (s, 3H). MS (M = 210) *m/z* (%): 210(10, M^+); 195 (100, $M^+ - 15$); 151(20); 139(13); 121(13); 77(29); 61(11); 45(14).

3.4. Diethyl 3-methyl-3-octyl-3-silaglutarate (2b)

R_f = 0.50 (hexane/Et_2O: 1/1). Bp: 165–170°C/0.05 mmHg. IR (neat) (cm^{-1}): 2940; 2920; 2880; 1730 ($\nu_{C=O}$); 1470; 1410; 1380; 1260 (ν_{Si-C}); 1090; 1040; 860; 800 (ν_{Si-C}). ^1H NMR ($CDCl_3$, 200 MHz) δ (ppm): 4.15 (q, J = 7.1 Hz, 4H); 2.05 (s, 4H); 1.40–1.20 (m including at 1.23 t, J = 7.1 Hz, 18H); 0.95–0.85 (t br, J = 6.7 Hz, 3H); 0.80–0.65 (t br, J = 7.6 Hz, 2H); 0.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ (ppm): −4.99 (Si–CH_3); 13.91; 14.08; 22.37; 22.79; 23.80; 28.91; 29.00; 31.61; 33.1; 59.82 (O–CH_2–CH_3); 171.84 (*C*=O). ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ (ppm): −4.11. MS (M = 330) *m/z* (%): 330(0.3, M^+); 243(19); 201(14); 176(14); 175(100); 133(47); 89(21); 61(14). Anal. calcd. for $C_{17}H_{34}O_4Si$: C, 61.77; H, 10.37. Found: C, 61.52; H, 10.38%.

3.5. Diethyl 3-methyl-3-vinyl-3-silaglutarate (2c)

R_f = 0.57 (CH_2Cl_2/AcOEt: 9/1). Bp: 100–120°C/0.1 mmHg. IR (neat) (cm^{-1}): 2990; 1730 ($\nu_{C=O}$); 1600; 1460; 1410; 1360; 1250 (ν_{Si-C}); 1150; 1090; 1030; 1000; 950; 870; 810 (ν_{Si-C}). ^1H NMR ($CDCl_3$, 200 MHz) δ (ppm): 6.25–6.05 (m, 2H); 5.95–5.80 (m, 1H); 4.12 (q, J = 7.1 Hz, 4H); 2.1 (s, 4H); 1.25 (t, J = 7.1 Hz, 6H); 0.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ (ppm): −5.06 (Si–CH_3); 14.19 (O–CH_2–CH_3); 24.12 (Si–CH_2–C=O) 60.08 (O–CH_2–CH_3); 133.11; 134.82; 171.64 (*C*=O). ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ (ppm): −6.17. MS (M = 244) *m/z* (%): 215 (0.4, $M^+ - 29$); 157(55); 145(18); 133(40); 115(100); 87(33); 77(16); 61(35); 45(30). Anal. Calcd for $C_{11}H_{20}O_4Si$: C, 54.07; H, 8.25. Found: C, 54.35; H, 8.42%.

3.6. Diethyl 3-methyl-3-[2-(4-methylphenyl)ethyl]-3-silaglutarate (2d)

R_f = 0.45 (hexane/Et_2O: 1/1). IR (neat) (cm^{-1}): 2980; 2920; 1720 ($\nu_{C=O}$); 1510; 1440; 1400; 1360; 1250 (ν_{Si-C}); 1090; 1030; 900; 860; 800 (ν_{Si-C}). ^1H NMR ($CDCl_3$, 200 MHz) δ (ppm): 7.15–7.05 (m, 4H); 4.10 (q, J = 7.0 Hz, 4H); 2.70–2.65 (m, 2H); 2.30 (s, 3H); 2.00 (s, 4H); 1.35 (t, J = 7.0 Hz, 6H); 1.15–1.05 (m, 2H); 0.20 (s, 3H). ^{13}C NMR ($CDCl_3$, 50,3 MHz) δ (ppm): −4.82 (Si–CH_3); 14.27 (O–CH_2–CH_3); 15.96 (–Ph(*p* – CH_3)); 20.82 (Si–CH_2–CH_2–Ph); 23.90 (Si–CH_2–C=O); 28.56 (Si–CH_2–CH_2–Ph); 60.11 (O–CH_2–CH_3); 127.50; 128.87; 135.10; 140.78; 171.91 (*C*=O). MS (M = 336) *m/z* (%): 336(5, M^+); 248(37); 220(13); 208(16); 207(80); 192(11); 191(27); 177(14); 176(14); 175(90); 161(23); 134(12); 133(100); 117(10); 105(28); 103(10); 102(19); 101(13); 91(13); 89(33); 77(44); 74(17); 61(26). Anal. calcd. for $C_{18}H_{28}O_4Si$: C, 64.25; H, 8.39. Found: C, 64.33; H, 8.43%.

3.7. Diethyl 3-(2-exo-bicyclo[2,2,1]heptyl)-3-methyl-3-silaglutarate (2e)

R_f = 0.48 (hexane/Et_2O: 1/1). Bp: 140–150°C/0.1 mmHg. IR (neat) (cm^{-1}): 2940; 2860; 1720 ($\nu_{C=O}$); 1450; 1400; 1360; 1250 (ν_{Si-C}); 1140; 1090; 1030; 900; 870; 800 (ν_{Si-C}). ^1H NMR ($CDCl_3$, 200 MHz) δ (ppm): 4.10 (q, J = 7.1 Hz) and 4.09 (q, J = 7.1 Hz) (4H); 2.32–2.19 (m, 2H); 2.01 (s, 2H); 1.96 (s, 2H); 1.61–1.49 (m, 2H); 1.49–1.38 (m, 2H); 1.33–1.09 (m including at 1.24 t, J = 7.1 Hz, 10H); 0.78 (dd, J = 9.8 and 7.4 Hz, 1H); 0.17 (s, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): −5.89 (Si–CH_3); 14.24 (O–CH_2–CH_3); 23.20 (Si–CH_2–CO); 23.39 (Si–CH_2–CO); 27.15; 28.37; 32.26; 33.94; 36.60; 37.45; 37.91; 60.02 (–OCH_2–CH_3); 172.15 (*C*=O); 172.19 (*C*=O). MS (M = 312) *m/z* (%): 225 (2.5, $M^+ - 87$); 204(11); 162(14); 161(100); 105(34); 89(11); 77(43); 61(20). Anal. calcd. for $C_{16}H_{28}O_4Si$: C, 61.11; H, 9.61. Found: C, 61.67; H, 9.25%.

3.8. Diethyl 3-allyl-3-phenyl-3-silaglutarate (2f)

R_f = 0.53 (hexane/Et_2O: 1/1). Bp: 160–165°C/0.1 mmHg. IR (neat) (cm^{-1}): 3080; 2970; 2920; 1720 ($\nu_{C=O}$); 1630; 1580; 1460; 1440; 1430; 1400; 1360; 1250 (ν_{Si-C}); 1150; 1100; 1030; 1020; 990; 920; 900; 860; 800 (ν_{Si-C}); 720; 700. ^1H NMR ($CDCl_3$, 200 MHz) δ (ppm): 7.70–

7.60 (m, 2H); 7.45–7.35 (m, 3H); 5.90–5.70 (m, 1H); 5.10–4.90 (m, 2H); 4.05 (q, $J = 7.1$ Hz, 4H); 2.30 (s, 4H); 2.05 (d, $J = 8.5$ Hz, 2H); 1.15 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 14.01 (O–CH_2–CH_3); 20.00 (Si–CH_2–CH=CH_2); 22.33 (Si–CH_2–C=O); 60.14 (O–CH_2–CH_3); 115.60 (Si–CH_2–CH=CH_2); 127.80; 130.02; 132.13 (Si–CH_2–CH=CH_2); 132.25; 133.98; 171.42 (C=O). (M = 320) m/z (%): 275 (0.5, $M^+ - 45$); 237(45); 233 (19, $M^+ - 87$); 195(100); 196(17); 151(12); 139(16); 123(12); 105(15); 91(11); 45(12). Anal. calcd. for $C_{17}H_{24}O_4Si$: C, 63.72; H, 7.56. Found: C, 63.57; H, 7.36%.

3.9. Diethyl 3,3-tetramethylene-3-silaglutarate (2g)

$R_f = 0.41$ (hexane/Et_2O: 1/1). Bp: 105–115°C/0.1 mmHg. IR (neat) (cm^{-1}): 3000; 2950; 2870; 1720 ($\nu_{C=O}$); 1455; 1410; 1430; 1370; 1250 (ν_{Si-C}); 1150; 1100; 1035; 875; 835 (ν_{Si-C}). ^1H NMR ($CDCl_3$, 250 MHz) δ (ppm): 4.11 (q, $J = 7.2$ Hz, 4H); 2.09 (s, 4H); 1.67–1.50 (m, 4H); 1.25 (t, $J = 7.2$ Hz, 6H); 0.87–0.68 (m, 4H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm): 10.15 (Si–CH_2–CH_2); 14.20 (O–CH_2–CH_3); 23.78 (Si–CH_2–C=O); 26.57 (Si–CH_2–CH_2); 60.04 (O–CH_2–CH_3); 171.60 (C=O). MS (M = 258) m/z (%): 229 (1.7, $M^+ - 29$); 216(14); 201(40); 188(17); 187(16); 174(24); 173(16); 172(22); 171(100, $M^+ - 87$); 170(14); 160(13); 159(45); 146(27); 145(17); 143(10); 135(13); 132(13); 131(27); 129(71); 128(13); 127(17); 119(11); 118(38); 117(23); 103(28); 102(10); 101(54); 100(13); 99(34); 98(13); 97(11); 91(12); 90(12); 89(23); 87(23); 86(12); 85(13); 83(22); 80(11); 77(12); 73(37); 71(12); 70(11); 69(13); 63(17); 55(12); 45(32). Anal. calcd. for $C_{12}H_{22}O_4Si$: C, 55.78; H, 8.58. Found: C, 55.48; H, 8.46%.

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