

Radical addition of tetrahydrofuran and tetrahydro-2-furanone to alkenylsilanes in the presence of di(*t*-butyl)peroxide

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Abstract

β -(Silylethyl)- and γ -(silylpropyl)-tetrahydrofurans and tetrahydro-2-furanones containing alkyl and phenyl groups at the Si atom were obtained by the reactions of tetrahydrofuran (THF) and tetrahydro-2-furanone with vinyl- and allylsilanes in the presence of di(*t*-butyl) peroxide (DTBP). To reduce the amount of bis-products, the ratio [heterocycle] : [alkenylsilane] : [DTBP] = 80 : 4 : 1 was used.

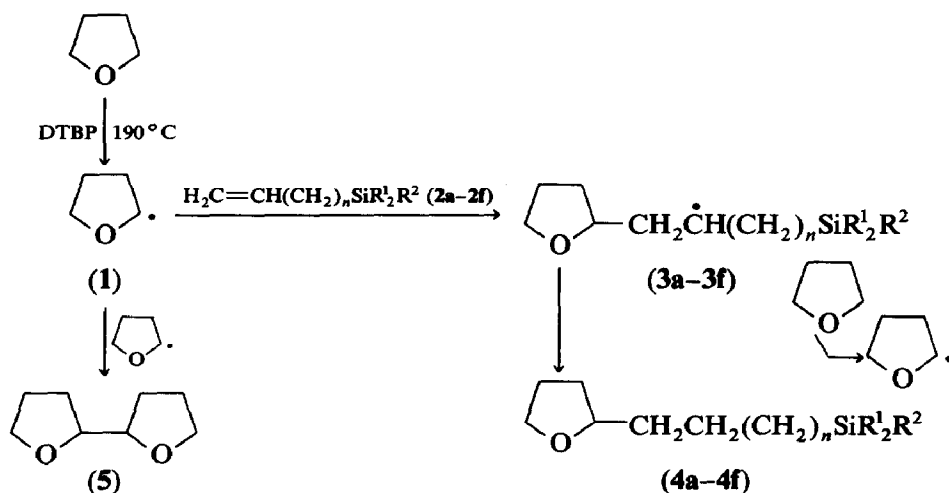
Introduction

Data on organosilicon derivatives of tetrahydrofuran and tetrahydro-2-furanone having an organosilicon group separated from the heterocycle by a carbon chain are very limited [1,2]. Further the synthetic procedures are multi-step and labour-intensive. It is known from the literature that THF [3,4] and tetrahydro-2-furanone [5] can add to alkenes under radical-reaction conditions. This prompted us to investigate similar reactions with vinyl- and allylsilanes, which if successful, would provide a convenient one-step route to organosilicon tetrahydrofuran and tetrahydro-2-furanone derivatives having an alkylsilyl group separated from the heterocycle by two or three methylene groups.

Since phenylhydrosilanes can undergo various transformations in the presence of DTBP [6], we first examined the behaviour of phenylvinylsilanes $\text{H}_2\text{C}=\text{CHSi-Ph}_n\text{Me}_{3-n}$, $n = 1-3$ (**2**) under typical radical-reaction conditions (25 M% DTBP, 160 °C, 3 h). It was found that the phenylvinylsilanes **2** do not undergo transformations under these conditions. Thus, not only alkylvinylsilanes, but also phenylvinylsilanes can be used in addition reactions.

Results and discussion

The data show that THF reacts with vinyl- and allylsilanes in the presence of DTBP to afford the corresponding 2-(silylalkyl)-tetrahydrofurans **4a–4f** (Scheme 1,



Scheme 1. $n = 0$: $\text{R}^1 = \text{R}^2 = \text{Me}$ (a); $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Ph}$ (b); $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$ (c); $\text{R}^1 = \text{R}^2 = \text{Ph}$ (d); $\text{R}^1 = \text{R}^2 = \text{Et}$ (e); $n = 1$: $\text{R}^1 = \text{R}^2 = \text{Me}$ (f).

Table 1). Thus a number of novel compounds, namely, 2-[β -(trimethylsilyl)ethyl]tetrahydrofuran (4a), 2-[β -(dimethylphenylsilyl)ethyl]tetrahydrofuran (4b), 2-[β -(methyldiphenylsilyl)ethyl]tetrahydrofuran (4c), 2-[β -(triphenylsilyl)ethyl]tetrahydrofuran (4d), 2-[β -(triethylsilyl)ethyl]tetrahydrofuran (4e) and 2-[γ -(trimethylsilyl)propyl]tetrahydrofuran (4f) were obtained.

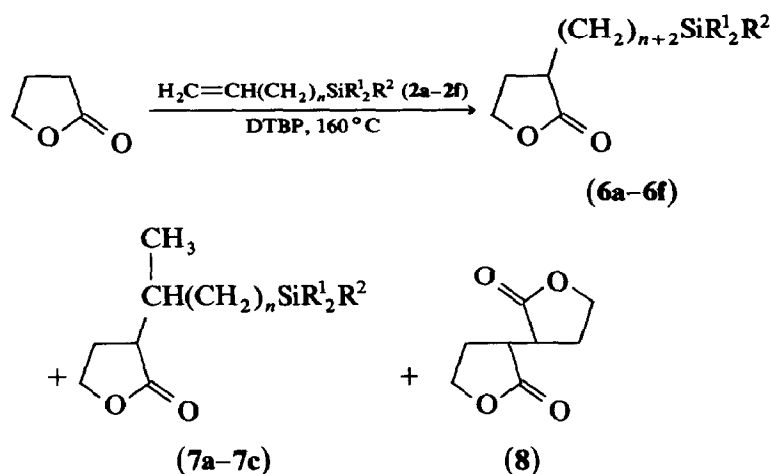
The reaction which gives 3 is initiated by the thermal decomposition of DTBP since this yields the t-butoxy radicals, which in turn generate the tetrahydrofuryl radical (1) that adds to vinyl- or allylsilane (2) to give the silylalkyl radical 3. However radical 3 can also add to the double bond of vinyl- or allylsilane; to avoid this, the reactions were carried out in a twenty-fold excess of THF. But, for a, e, f in addition to reaction product 4, small amounts (5–8%) of unidentified compounds were detected; the GC/MS spectrometry data show that they are products of the addition of 3 to alkenylsilane. In addition, even with a comparatively small quantity of DTBP determining the amount of free radicals in the reaction mixture, an

Table 1

Synthesis of 2-(silylalkyl)tetrahydrofurans 4 (190 °C, 2 h, [THF]:[2]:[DTBP] = 80:4:1)

Alkenylsilane (2)	Products	
	2-(Silylalkyl)tetrahydrofuran 4 (yield, %)	Bis(2-tetrahydrofuryl) 5 (yield, %) ^a
(a) $\text{H}_2\text{C}=\text{CHSiMe}_3$	90	4
(b) $\text{H}_2\text{C}=\text{CHSiMe}_2\text{Ph}$	87	5
(c) $\text{H}_2\text{C}=\text{CHSiMePh}_2$	83	1
(d) $\text{H}_2\text{C}=\text{CHSiPh}_3$	89	—
(e) $\text{H}_2\text{C}=\text{CHSiEt}_3$	85	12
(f) $\text{H}_2\text{C}=\text{CHCH}_2\text{SiMe}_3$	56	30

^a GLC data.



Scheme 2. $n = 0$: $\text{R}^1 = \text{R}^2 = \text{Me}$ (a); $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Ph}$ (b), $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$ (c) $\text{R}^1 = \text{R}^2 = \text{Ph}$ (d); $\text{R}^1 = \text{R}^2 = \text{Et}$ (e); $n = 1$: $\text{R}^1 = \text{R}^2 = \text{Me}$ (f).

appreciable quantity (up to 30%) of bis(2-tetrahydrofuryl) (5) was detected among the reaction products.

Further experiments show that tetrahydro-2-furanone, like THF, adds to vinyl- and allylsilanes in the presence of DTBP (Scheme 2, Table 2). Thus the novel compounds, 3-[β -(trimethylsilyl)ethyl]tetrahydro-2-furanone (6a), 3-[β -(dimethylphenylsilyl)ethyl]tetrahydro-2-furanone (6b), 3-[β -(methyldiphenylsilyl)ethyl]tetrahydro-2-furanone (6c), 3-[β -(triphenylsilyl)ethyl]tetrahydro-2-furanone (6d), 3-[β -(triethylsilyl)ethyl]tetrahydro-2-furanone (6e) and 3-[γ -(trimethylsilyl)propyl]tetrahydro-2-furanone (6f), were obtained.

Apart from the main products 6a–6f, bis(3-tetrahydro-2-furanonyl) (8) was also found in the reaction mixture for a, e, f.

The syntheses of the 3-(silylalkyl)-tetrahydro-2-furanones 6a–6f were performed at 160 °C to avoid thermolysis of the lactone cycle. It is noteworthy that in the case of a, b, c, apart from the main product 6a, 6b and 6c, the α -addition products of tetrahydro-2-furanone to alkenylsilanes 7a–7c were also detected. The amount of the α -product diminishes with the increasing number of phenyl groups at the Si atom (Table 3).

Table 2

Synthesis of the 3-(silylalkyl)-tetrahydro-2-furanones, 6a–6f (160 °C, [tetrahydro-2-furanone] : [2] : [DTBP] = 80 : 4 : 1)

Alkenylsilane (2)	Time (h)	Product	Yield (%)	Bis-(3-tetrahydro- 2-furanonyl) (8) (yield, %)
(a) $\text{H}_2\text{C}=\text{CHSiMe}_3$	4	6a	52	18
(b) $\text{H}_2\text{C}=\text{CHSiMe}_2\text{Ph}$	7	6b	17	–
(c) $\text{H}_2\text{C}=\text{CHSiMePh}_2$	7	6c	13	–
(d) $\text{H}_2\text{C}=\text{CHSiPh}_3$	7	6d	22	–
(e) $\text{H}_2\text{C}=\text{CHSiEt}_3$	4	6e	46	22
(f) $\text{H}_2\text{C}=\text{CHCH}_2\text{SiMe}_3$	4	6f	29	32

Table 3

Relative content of α -products resulting from the addition of tetrahydro-2-furanone to alkenylsilanes

Alkenylsilane (2)	Number of Me groups in 2	Number of Ph groups in 2	Amount of α -product (ratio 7:6) ^a
(a) $\text{H}_2\text{C}=\text{CHSiMe}_3$	3	0	33:67
(b) $\text{H}_2\text{C}=\text{CHSiMe}_2\text{Ph}$	2	1	25:75
(c) $\text{H}_2\text{C}=\text{CHSiMePh}_2$	1	2	1:99
(d) $\text{H}_2\text{C}=\text{CHSiPh}_3$	0	3	0:100

^a ^1H NMR data.

It can be assumed that the bulky phenyl groups at the Si atom sterically prevent the formation of the α -product.

Thus a convenient route to organosilicon tetrahydrofuran and tetrahydro-2-furanone derivatives having an organosilicon group separated from the heterocycle by a carbon chain has been developed.

Experimental

Trimethyl- (2a), triethylvinylsilane (2e), trimethylallylsilane (2f) and DTBP were purchased from Fluka and used without further purification. Dimethylphenyl- (2b), methyldiphenyl- (2c) and triphenylvinylsilane (2d) were obtained by standard procedures [7]. THF and tetrahydro-2-furanone were dried and purified immediately before use by distillation over CaCl_2 .

The ^1H , ^{13}C and ^{29}Si NMR spectra were recorded with WH-90/DS and WM-360 instruments (Bruker) in CDCl_3 solutions with TMS as internal standard. Mass spectra were recorded with a Kratos MS-25 GC/MS 70 eV system. IR spectra were recorded with a Perkin Elmer spectrometer (580 V). The IR spectra of solid substances were obtained from their suspension in Nujol, those of liquids – from a thin layer.

Reactions were monitored by GLC analysis of the reaction mixtures by use of a Chrom-5 instrument (Czechoslovakia) with a flame-ionization detector and a glass column (1.2 m $\times$ 3 mm) packed with 5% OV on Chromosorb W-AW (80–100 mesh), helium was the carrier gas (30 ml/min). Thin-layer chromatography on Silufol UV_{254} plates was also used for this purpose.

Synthesis of 2-silylalkyltetrahydrofurans 4a–4f (General procedure)

A mixture of 1.6 M THF, 0.08 M alkenylsilane and 0.02 M DTBP (80:4:1 ratio) were placed in a steel autoclave and heated for 2 h at 190°C. The products were purified by distillation under vacuum (4a, 4b, 4e, 4f) or by column chromatography (4c, 4d) on silica gel $\text{L}_{40/100}$ with 2–15% ethyl acetate in hexane as eluent.

Synthesis of 3-silylalkyltetrahydro-2-furanones 6a–6f (General procedure)

The alkenylsilane (2) (0.08 M) was added to a mixture of 1.6 M tetrahydro-2-furanone and 0.02 M DTBP (80:4:1 ratio) at 160°C during 2 h (6a, 6c, 6f) or 5 h (6b, 6d, 6e) and the heating was continued for another 2 h. The products were purified

by distillation under vacuum (6a, 6c, 6f) or by column chromatography (6b, 6d, 6e) on silica gel L_{40/100} with 10–20% ethyl acetate in hexane as eluent.

2-[β -(Trimethylsilyl)ethyl]tetrahydrofuran (4a), b.p. 112–113°C/8 mmHg, n_D^{20} = 1.4455. Mass spectrum, m/e (rel. intensity (%)): 157 (M^+ – Me, 17), 129(4), 127(7), 116(7), 115(5), 103(5), 101(18), 99(11), 89(6), 85(4), 82(3), 81(4), 77(4), 76(5), 75(66), 74(7), 73(86), 72(8), 71(100), 70(10), 67(15), 59(17), 54(17), 45(17), 43(36). ^1H NMR: δ (ppm): 0.00(s, 9H, SiMe₃), 0.46(m, 1H, SiCH₂), 0.59(m, 2H, SiCH₂), 1.43(m, 1H), 1.89(m, 2H), 1.98(m, 1H), 3.75 (m, 2H, 5-CH₂), 3.88(m, 1H, 2-CH₂). ^{13}C NMR: δ (ppm): –1.75, 12.83, 25.83, 29.90, 30.95, 67.64, 81.79.

2-[β -(Dimethylphenylsilyl)ethyl]tetrahydrofuran (4b), b.p. 120–122°C/4 mmHg. Mass spectrum, m/e (rel. intensity (%)): 219(M^+ – Me, 23), 163(10), 157(45), 137(52), 136(18), 135(100), 128(29), 121(20), 119(10), 107(13), 105(24), 91(14), 75(22), 71(47), 59(11), 43(38), 41(13). ^1H NMR: δ (ppm): 0.30(s, 6H, SiMe₂), 0.69–0.95 (m, 2H, SiCH₂), 1.38–2.02(m, 5H, SiCH₂CH₂; 3, 4CH₂), 3.71–3.91 (m, 3H, OCH₂, OCH), 7.33–7.59(m, 5H, SiPh). ^{13}C NMR: δ , (ppm): –3.29, –3.21, 11.79, 25.65, 29.66, 30.72, 67.61, 81.63, 127.66, 128.74, 133.49, 139.12. ^{29}Si NMR: δ (ppm): –2.61.

2-[β -(methyldiphenylsilyl)ethyl]tetrahydrofuran (4c). Mass spectrum, m/e (rel. intensity (%)): 281(M^+ – Me, 6), 220(24), 219(98), 199(30), 198(25), 197(100), 195(14), 190(20), 184(11), 182(17), 157(42), 121(16), 119(12), 105(39), 91(12), 71(38), 53(14), 43(29), 41 (15). ^1H NMR, δ (ppm): 0.53(s, 3H, SiMe), 0.78–2.17(m, 8H), 3.46–4.00(m, 3H, OCH₂, OCH), 7.14–7.70(m, 10H, SiPh₂). ^{13}C NMR: δ (ppm): –4.42, 10.49, 25.81, 29.80, 30.90, 67.74, 81.68, 127.91, 129.20, 134.59, 137.23. ^{29}Si NMR: δ (ppm): –6.84.

2-[β -(Triphenylsilyl)ethyl]tetrahydrofuran (4d). Mass spectrum, m/e (rel. intensity (%)): 281(M^+ – Ph, 100), 260(25), 259 (100), 252(10), 199(18), 181(22), 155(5), 105(7), 71(7). ^1H NMR: δ , ppm: 0.71–2.44(m, 8H), 3.49–4.00(m, 3H, OCH₂, OCH), 6.84–7.78(m, 15H, SiPh₃). ^{13}C NMR: δ (ppm): 9.65, 25.89, 29.99, 30.98, 67.79, 81.76, 128.01, 129.55, 135.20, 135.80. ^{29}Si NMR: δ (ppm): –10.41.

2-[β -(Triethylsilyl)ethyl]tetrahydrofuran (4e), b.p. 70°C/1 mmHg, n_D^{20} = 1.4592. Mass spectrum, m/e (rel. intensity (%)): 186 (M^+ – C₂H₄, 12), 185(70), 171(14), 157(30), 155(19), 143(12), 141(6), 129 (35), 117(14), 116(49), 115(14), 113(14), 103(95), 101(19), 99(19), 89 (44), 87(58), 81(14), 75(100), 73(17), 71(26), 61(19), 59(42), 58(8), 57(9), 55(9), 47(8), 43(9). ^1H NMR: δ (ppm), J (Hz): 0.42–0.66(m, 2H, SiCH₂CH₂), 0.51(q, 6H, J = 7.9, SiCH₂CH₃), 0.94(t, 9H, J = 7.9, SiCHCH₃), 1.42(m, 2H), 1.60(m, 1H), 1.88(m, 2H), 1.99(m, 1H), 3.73(m, 2H, 5-CH₂), 3.87(m, 1H, 2-CH). ^{13}C NMR: δ (ppm): 3.45, 7.47, 9.30, 25.88, 29.95, 31.03, 67.72, 82.12.

2-[γ -(Trimethylsilyl)propyl]tetrahydrofuran (4f), b.p. 85–86°C/10 mmHg, n_D^{20} = 1.4435. Mass spectrum, m/e (rel. intensity (%)): 171(M^+ – Me, 24), 143(12), 141(6), 129(6), 116(7), 115(6), 113(6), 103(20), 101(17), 99(5), 96(6), 95(5), 89(14), 81(12), 79(6), 76(5), 71(100), 68(16), 67(17), 59(20), 45(15), 43(26). ^1H NMR: δ (ppm): 0.07(s, 9H, SiMe₃), 0.44(m, 2H, SiCH₂), 1.42(m, 5H), 1.83(m, 3H), 3.72(m, 3H). ^{13}C NMR: δ (ppm): –1.64, 14.21, 25.10, 28.23, 42.08, 66.64, 179.49.

3-[β -(Trimethylsilyl)ethyl]tetrahydro-2-furanone (6a), b.p. 98°C/1 mmHg, n_D^{20} = 1.4535. IR(cm^{–1}): 1775(ν (C=O)). Mass spectrum, m/e (rel. intensity (%)): 171 (M^+ – Me, 14), 159(5), 158(35), 157(14), 103(23), 99(21), 91(8), 85(10), 75(37), 73(100), 59(22), 57(7). ^1H NMR: δ , ppm: 0.02(s, 9H, SiMe₃), 0.58(m, 2H, SiCH₂),

1.50(m,1H,3-CH), 1.91(m,2H), 2.40(m,1H), 2.52(m,1H), 4.21(m,1H,5-CH₂), 4.35(m,1H,5-CH₂). ¹³C NMR: δ (ppm): -1.51, 16.61, 21.94, 28.79, 34.29, 39.06, 66.57, 179.57.

3-[β -(Dimethylphenylsilyl)ethyl]tetrahydro-2-furanone (**6b**). IR (cm⁻¹): 1772(ν (C=O)). Mass spectrum, m/e (rel. intensity (%)): 233(M^+ - Me,44), 220(16), 218(10), 171(31), 137(18), 136(14), 135(100), 107(10), 105(18), 91(10), 59(11), 53(11), 43(28), 41(12), 28(17). ¹H NMR: δ (ppm): 0.29(s,6H,SiMe₂), 0.51-1.09(m,2H,SiCH₂), 1.16-2.73(m,5H), 3.89-4.44(m,2H,OCH₂), 7.13-7.67(m,5H,SiPh). ¹³C NMR: δ (ppm): -3.20, 13.27, 24.89, 28.05, 41.80, 66.39, 127.96, 129.12, 133.59, 138.69, 179.17. ²⁹Si NMR: δ (ppm): -2.78.

3-[β -(Methyldiphenylsilyl)ethyl]tetrahydro-2-furanone (**6c**). IR (cm⁻¹): 1771(ν (C=O)). Mass spectrum, m/e (rel. intensity (%)): 295(M^+ - Me,10), 234(20), 233(100), 199(10), 198(20), 197(97), 195(13), 183 (10), 181(14), 137(13), 121(21), 119(12), 105(35), 93(11), 77(11), 53 (16), 43(14), 41(14), 32(11), 28(25). ¹H NMR: δ (ppm): 0.56(s,3H,SiMe), 0.76-2.78(m,7H), 3.96-4.16(m,2H, OCH₂), 7.02-7.71(m,10H,SiPh₂). ¹³C NMR: δ (ppm): -4.58, 11.81, 24.83, 28.10, 41.77, 66.34, 128.01, 129.41, 134.51, 136.56, 179.00. ²⁹Si NMR: δ (ppm): -7.22.

3-[β -(Triphenylsilyl)ethyl]tetrahydro-2-furanone (**6d**). IR(cm⁻¹): 1758(ν (C=O)). Mass spectrum, m/e (rel. intensity (%)): 295(M^+ - Ph, 100), 266(18), 259(74), 252(10), 199(8), 181(17), 155(4), 105(7), 71(7). ¹H NMR: δ (ppm): 1.15-2.78(m,7H), 3.96-4.44(m,2H,OCH₂), 7.07-7.87(m,15H,SiPh₃). ¹³C NMR: δ (ppm): 10.81, 24.91, 28.04, 41.73, 66.27, 128.03, 129.62, 134.56, 135.64, 178.88. ²⁹Si NMR: δ (ppm): -10.94.

3-[β -(Triethylsilyl)ethyl]tetrahydro-2-furanone (**6e**), b.p. 129-131°C/1 mmHg, $n_D^{20} = 1.4702$. IR(cm⁻¹): 1770(ν (C=O)). Mass spectrum, m/e (rel. intensity (%)): 199(M^+ - Et,100), 171(13), 143(10), 127(18), 117(7), 115(32), 113(20), 103(38), 99(23), 87(58), 65(35), 59(44). ¹H NMR: δ (ppm), J (Hz): 0.53(q,6H, $J = 7.9$, SiCH₂CH₃), 0.58(m,2H,SiCH₂CH₂), 0.93(t,9H, $J = 7.9$,SiCH₂CH₃), 1.59(m,1H,3 - CH), 1.91(m,2H), 2.40(m,1H), 2.52(m,1H), 4.21(m,1H,5-CH₂), 4.35(m,1H,5-CH₂). ¹³C NMR: δ (ppm): 3.32, 7.42, 8.82, 24.92, 28.07, 42.12, 66.47, 179.25.

3-[γ -(Trimethylsilyl)propyl]tetrahydro-2-furanone (**6f**), b.p. 103°C/1 mmHg, $n_D^{20} = 1.4559$. IR(cm⁻¹): 1775(ν (C=O)). Mass spectrum, m/e (rel. intensity (%)): 200 (M^+ ,4), 199(M^+ - H,19), 185(20), 172(10), 171(55), 157(9), 129(5), 127(6), 115(5), 103(11), 99(15), 87(10), 86(12), 85(8), 81(5), 75(40), 74(8), 73(100), 59(21), 45(13). ¹H NMR: δ (ppm): -0.02 (s,9H,SiMe₃), 0.53(m,2H,SiCH₂), 1.42(m,2H,SiCH₂CH₂), 1.50(m,1H,3-CH), 1.91(m,2H), 2.40(m,1H), 2.52(m,1H), 4.21(m,1H,5-CH₂), 4.35(m,1H,5-CH₂). ¹³C NMR: δ (ppm): -1.51, 16.61, 21.94, 28.79, 34.29, 39.06, 66.57, 179.57.

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