Journal of Organometallic Chemistry, 393 (1990) 333–338
Elsevier Sequoia S.A., Lausanne
JOM 20902

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

Vladimir Gevorgyan, Einārs Priede, Edvards Liepiņš, Māris Gavars and Edmunds Lukevics *

Institute of Organic Synthesis, Latvian Academy of Sciences, Riga (U.S.S.R.)

(Received March 15th, 1990)

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.

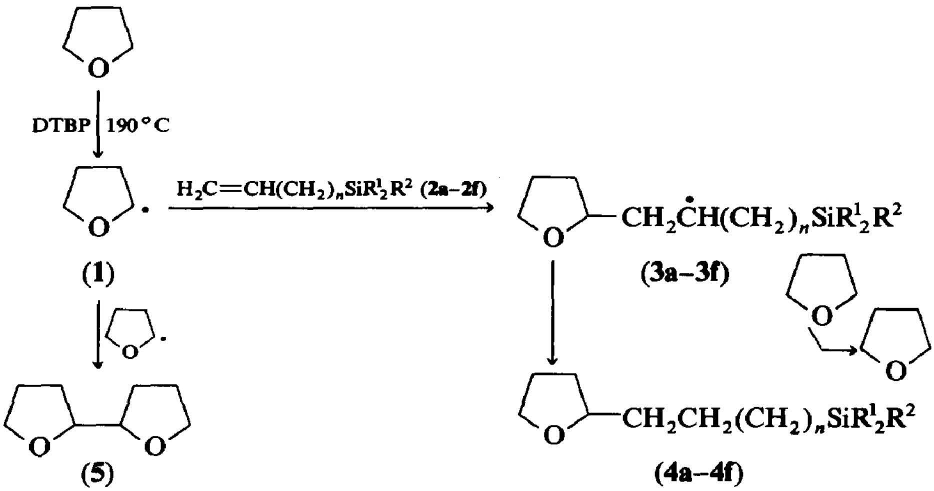
Introduction

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 $H_2C{=}CHSiPh_nMe_{3-n}$, $n = 1$–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. $n = 0$: $R^1 = R^2 = Me$ (**a**); $R^1 = Me$, $R^2 = Ph$ (**b**); $R^1 = Ph$, $R^2 = Me$ (**c**); $R^1 = R^2 = Ph$ (**d**); $R^1 = R^2 = Et$ (**e**); $n = 1$: $R^1 = R^2 = Me$ (**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.

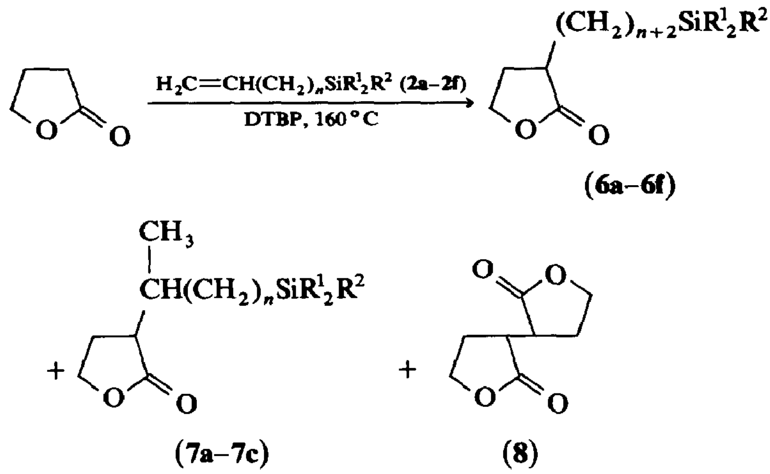
The reaction which gives **3** is initiated by the thermal decomposition of DTBP since this yields the t-butoxy radicals, which in turn generate the tetrahydrofuryl radical (**1**) that adds to vinyl- or allylsilane (**2**) to give the silylalkyl radical **3**. However radical **3** can also add to the 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**) $H_2C{=}CHSiMe_3$	90	4
(**b**) $H_2C{=}CHSiMe_2Ph$	87	5
(**c**) $H_2C{=}CHSiMePh_2$	83	1
(**d**) $H_2C{=}CHSiPh_3$	89	–
(**e**) $H_2C{=}CHSiEt_3$	85	12
(**f**) $H_2C{=}CHCH_2SiMe_3$	56	30

[a] GLC data.



Scheme 2. $n=0$: $R^1=R^2=Me$ (**a**); $R^1=Me$, $R^2=Ph$ (**b**), $R^1=Ph$, $R^2=Me$ (**c**) $R^1=R^2=Ph$ (**d**); $R^1=R^2=Et$ (**e**); $n=1$: $R^1=R^2=Me$ (**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**) $H_2C{=}CHSiMe_3$	4	**6a**	52	18
(**b**) $H_2C{=}CHSiMe_2Ph$	7	**6b**	17	–
(**c**) $H_2C{=}CHSiMePh_2$	7	**6c**	13	–
(**d**) $H_2C{=}CHSiPh_3$	7	**6d**	22	–
(**e**) $H_2C{=}CHSiEt_3$	4	**6e**	46	22
(**f**) $H_2C{=}CHCH_2SiMe_3$	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**) $H_2C{=}CHSiMe_3$	3	0	33:67
(**b**) $H_2C{=}CHSiMe_2Ph$	2	1	25:75
(**c**) $H_2C{=}CHSiMePh_2$	1	2	1:99
(**d**) $H_2C{=}CHSiPh_3$	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 × 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 $L_{40/100}$ 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). ^{1}H NMR: δ (ppm): 0.00(s,9H,$SiMe_3$), 0.46(m,1H,$SiCH_2$), 0.59(m,2H,$SiCH_2$), 1.43(m,1H), 1.89(m,2H), 1.98(m,1H), 3.75 (m,2H,5-CH_2), 3.88(m,1H,2-CH_2). ^{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). ^{1}H NMR: δ (ppm): 0.30(s,6H,$SiMe_2$), 0.69–0.95 (m,2H,$SiCH_2$), 1.38–2.02(m,5H,$SiCH_2CH_2$;3,4CH_2), 3.71–3.91 (m,3H,OCH_2, 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). ^{1}H NMR, δ (ppm): 0.53(s,3H,SiMe), 0.78–2.17(m,8H), 3.46–4.00(m,3H,OCH_2,OCH), 7.14–7.70(m,10H,$SiPh_2$). ^{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). ^{1}H NMR: δ, ppm: 0.71–2.44(m,8H), 3.49–4.00(m,3H,OCH_2,OCH), 6.84–7.78(m,15H,$SiPh_3$). ^{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^+ – C_2H_4,12), 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). ^{1}H NMR: δ (ppm), J (Hz): 0.42–0.66(m,2H,$SiCH_2CH_2$), 0.51(q, 6H, J = 7.9, $SiCH_2CH_3$), 0.94(t,9H,J = 7.9,$SiCHCH_3$), 1.42(m,2H), 1.60(m,1H), 1.88(m,2H), 1.99(m,1H), 3.73(m,2H,5-CH_2), 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). ^{1}H NMR: δ (ppm): 0.07(s,9H,$SiMe_3$), 0.44(m,2H,$SiCH_2$), 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). ^{1}H NMR: δ, ppm: 0.02(s,9H,$SiMe_3$), 0.58(m,2H,$SiCH_2$), 1.50(m,1H,3-CH), 1.91(m,2H), 2.40(m,1H), 2.52(m,1H), 4.21(m,1H,5-CH$_2$), 4.35(m,1H,5-CH$_2$). ^{13}C 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). ^{1}H NMR: δ (ppm): 0.29(s,6H,SiMe$_2$), 0.51–1.09(m,2H,SiCH$_2$), 1.16–2.73(m,5H), 3.89–4.44(m,2H,OCH$_2$), 7.13–7.67(m,5H,SiPh). ^{13}C 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. ^{29}Si 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). ^{1}H NMR: δ (ppm): 0.56(s,3H,SiMe), 0.76–2.78(m,7H), 3.96–4.16(m,2H, OCH$_2$), 7.02–7.71(m,10H,SiPh$_2$). ^{13}C 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. ^{29}Si 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). ^{1}H NMR: δ (ppm): 1.15–2.78(m,7H), 3.96–4.44(m,2H,OCH$_2$), 7.07–7.87(m,15H,SiPh$_3$). ^{13}C NMR: δ (ppm): 10.81, 24.91, 28.04, 41.73, 66.27, 128.03, 129.62, 134.56, 135.64, 178.88. ^{29}Si 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). ^{1}H NMR: δ (ppm), *J* (Hz): 0.53(q,6H,J = 7.9, SiCH_2CH$_3$), 0.58(m,2H,SiCH_2CH$_2$), 0.93(t,9H,J = 7.9,SiCH$_2$$\mathit{CH}_3$), 1.59(m,1H,3 − CH), 1.91(m,2H), 2.40(m,1H), 2.52(m,1H), 4.21(m,1H,5-CH$_2$), 4.35(m,1H,5-CH$_2$). ^{13}C 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). ^{1}H NMR: δ (ppm): −0.02 (s,9H,SiMe$_3$), 0.53(m,2H,SiCH_2), 1.42(m,2H,SiCH$_2$$\mathit{CH}_2$), 1.50(m,1H,3-CH), 1.91(m,2H), 2.40(m,1H), 2.52(m,1H), 4.21(m,1H,5-CH$_2$), 4.35(m,1H,5-CH$_2$). ^{13}C NMR: δ (ppm): −1.51, 16.61, 21.94, 28.79, 34.29, 39.06, 66.57, 179.57.

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