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SYNTHESIS OF 2-(4,5-DIHYDROFURYL)- AND 2-(TETRAHYDROFURYL)-DIMETHYLHYDROSILANES. REARRANGEMENT OF 2-(TETRAHYDROFURYL)-DIMETHYLHYDROSILANE WITH RING EXPANSION

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Abstract - 2-(4,5-Dihydrofuryl)- and 2-(tetrahydrofuryl)dimethylhydrosilanes (I and II) have been synthesized. The latter rearranges easily and quantitatively to 1-oxa-2-sila-2,2-dimethylcyclohexane in the presence of palladium catalyst. The possibility of hydrosilylation of alkenes and alkynes by I and II has been demonstrated.

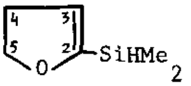
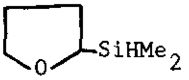
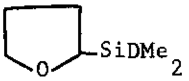
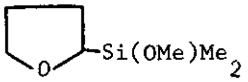
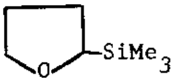
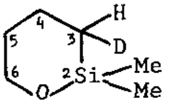
2-(4,5-Dihydrofuryl)- and 2-(tetrahydrofuryl)dimethylhydrosilanes have not been described in literature before. However, they may be useful for introduction of di- and tetrahydrofurylsilyl groups into unsaturated compounds by the hydrosilylation.

The 2-(4,5-dihydrofuryl)dimethylhydrosilane (I) has been prepared by metallation of 2,3-dihydrofurane with n-BuLi in THF at -30°C and subsequent reaction of obtained dihydrofuryllithium with dimethylchlorosilane at -45°C. The yield of I was 50%, bp 133.5°C/760 mm Hg, $n_D^{20} = 1.4495$, IR spectrum (cm^{-1}): 1600 ($\nu_{C=C}$), 2130 (ν_{Si-H}), for ^1H NMR and mass-spectral data of I see Table 1.

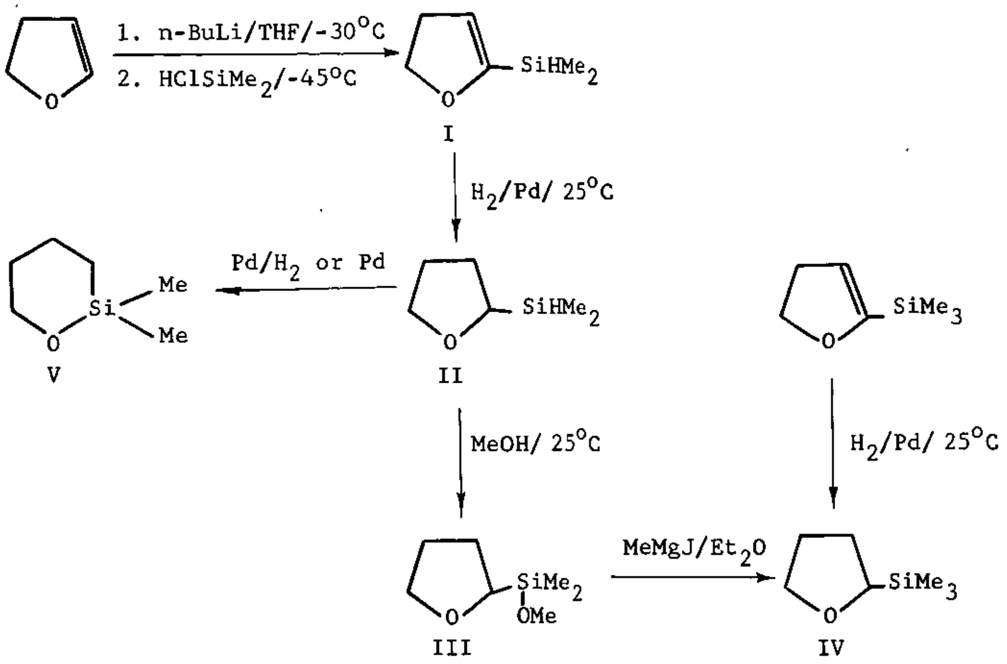
Liquid-phase heterogeneous hydrogenation of hydrosilane I (0,1 M pentane solution) gave quantitative yield of 2-(tetrahydrofuryl)dimethylhydrosilane (II) (bp 135°C/760 mm Hg, $n_D^{20} = 1.4362$, ν_{Si-H} 2120 cm^{-1}) under mild conditions (20°C, 1 atm. H_2, catalyst 5 wt.% Pd/Al_2O_3). The structure of II has been confirmed by ^1H NMR and mass-spectrum (Table 1) and also by the subsequent methanolysis (25°C, 10 min) and methylation (MeMgJ/ether) leading to 2-(tetrahydrofuryl)trimethylsilane (IV) (Table 1) identical with the product obtained from the hydrogenation of 2-(4,5-dihydrofuryl)trimethylsilane [1].

However, quite unexpectedly after the total conversion of I into II the latter under hydrogenation conditions turns out to be converted easily and quantitatively into previously described 1-oxa-2-sila-2,2-dimethylcyclohexane (V) [3].

Table 1

Compound	^{1}H NMR (90 MHz, CDCl$_3$), δ,ppm;J,Hz	MS (70 eV) m/e (rel.intensity, %)
	0.22(d,6H,J=3.6, SiMe$_2$), 2.61 (dt,2H,J_1=9.0,J_2=2.6,4-CH$_2$), 4.06(m,1H,SiH), 4.30(t,2H, J=9.0, 5-CH$_2$), 5.29(t,1H, J=2.6, 3-CH)	128(M$^+$,100), 113(96), 111(77), 99(14), 98(26), 85(33), 83(62), 72(20), 59(85)
	0.17(d,6H,J=4.4,SiMe$_2$), 1.86(m,4H, 3,4-CH$_2$), 3.33(m, 1H,2-CH), 3.79(m,3H,5-CH$_2$, SiH)	102(M$^+$-28,100), 101(28), 87(94), 85(11), 75(16), 72(10), 71(26), 61(16), 59(53), 58(16)
	0.07(m,6H,J_{H-D}=0.5,SiMe$_2$), 1.77(m,4H, 3,4-CH$_2$), 3.19(m, 1H,2-CH), 3.56(m,2H,5-CH$_2$)	103(M$^+$-28,100), 102(18), 101(14), 88(90), 87(34), 86(12), 75(16), 71(31), 62(15), 61(13), 60(55), 59(29), 58(21)
	0.15(s,3H,SiMe), 0.17(s,3H, SiMe), 1.86(m,4H, 3,4-CH$_2$), 3.21(m,1H,2-CH), 3.50(s,3H, OMe), 3.75(m,2H,5-CH$_2$)	132(M$^+$-28,11), 117(100), 89(53), 59(22)
	0.06(s,9H,SiMe$_3$), 1.85(m,4H, 3,4-CH$_2$), 3.23(m,1H,2-CH), 3.75(m,2H,5-CH$_2$)	129(M$^+$-15,2), 116(38), 101(100), 73(62), 59(36)
	0.07(s,6H,SiMe$_2$), 0.58(m,1H, 3-CHD), 1.53(m,2H,4-CH$_2$), 1.76(m,2H,5-CH$_2$), 3.79(m,2H, 6-CH$_2$)	131(M$^+$,9), 117(30), 116(100), 115(65), 113(15), 88(14), 87(71), 75(10), 59(10)

Moreover, it has been shown that II quantitatively is converted into V under the same conditions in the absence of hydrogen. We should stress that the formation of V from II does not take place until the starting hydrosilane I presents in the reaction mixture. It indicates the strong interaction between I and the catalyst thanks to which the preparative synthesis of the hydrosilane II becomes possible. To elucidate the mechanism of the rearrangement of II into V deuteroanalogue (II-d) of the hydrosilane II has been synthesized by the reduction of III using LiAlD$_4$. In the presence of the catalyst Pd/Al$_2$O$_3$ II-d rearranges into corresponding deuteroanalogue of V(V-d) containing the deuterium atom in the 3rd position of the ring. Thus, the rearrangement II→V proceeds evi-



dently through the hydride ion detachment stage by palladium catalyst from the hydrosilane II molecule with subsequent C-O bond cleavage and ring expansion according to the following scheme:

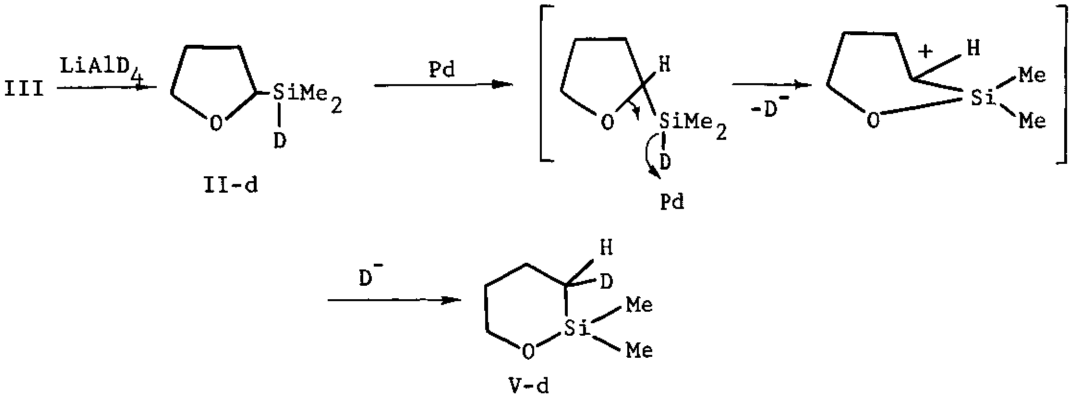


Table 2

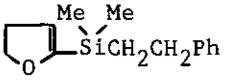
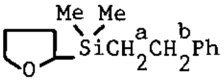
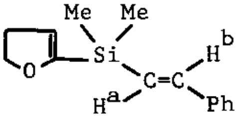
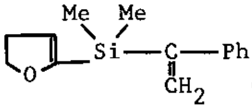
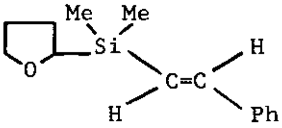
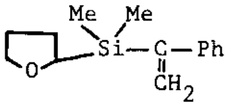
Hydro-silane	Alkene or alkyne	Hydrosilylation products (yield,%)	^{1}H NMR (δ,ppm; J,Hz)	MS, m/e (rel.intensity, %)
I	PhCH=CH$_2$	 (73)	0.15(S,6H,SiMe$_2$), 1.01(m,2H,a-CH$_2$), 2.58(dt,J$_1$=9.0,J$_2$=2.6,2H,4-CH$_2$),2.68 (m,2H,b-CH$_2$), 4.28 (t,J=9.0,2H,5-CH$_2$), 5.22(t,J=2.6,1H, 3-CH), 7.23(m,5H,Ph)	232(M$^+$,10), 204(23), 147(13), 135(11), 129(13), 128(100), 114(11), 113(99), 98(16), 97(42), 75(13), 72(24), 69(11), 59(29)
II	PhCH=CH$_2$	 (77)	0.04(S,3H,SiMe), 0.06(S,3H,SiMe), 0.96(m,2H,a-CH$_2$), 1.84(m,4H,3.4-CH$_2$), 2.69(m,2H,b-CH$_2$), 3.26(m,1H,2-CH), 3.73(m,2H,5-CH$_2$), 7.23(m,5H,Ph)	234(M$^+$,0.4), 206(27), 164(10), 163(49), 162(100), 147(43), 135(61), 102(19), 101(48), 75(11), 59(77)
I	PhC≡CH	 (77)	0.31(S,6H,SiMe$_2$), 2.60(dt,J$_1$=9.0,J$_2$=2.6,2H,4-CH$_2$), 4.31 (t,J=9.0,2H,5-CH$_2$), 5.28(t,J=2.6,1H, 3-CH), 6.45(d,1H, J=19.1,a-H),7.01(d, 1H,J=19.1,b-H),7.2-7.5(m,5H,Ph)	230(M$^+$,40), 215(22), 201(28), 187(23), 185(61), 155(21), 145(100), 128(29), 102(20), 89(66), 75(31), 59(77)
		 (9)	0.29(S,6H,SiMe$_2$), 2.60(dt,J$_1$=9.0,J$_2$=2.6,2H,4-CH$_2$),4.31 (t,J=9.0,2H,5-CH$_2$), 5.28(t,J=2.6,1H, 3-CH), 5.74(d,1H, J=2.8,C=CH), 5.96 (d,1H,J=2.8,C=CH), 7.2-7.5(m,5H,Ph)	230(M$^+$,100), 215(53), 187(17), 185(26), 162(12), 161(18), 159(20), 145(30), 135(41), 127(100), 97(87), 69(16), 59(19)
II	PhC≡CH	 (62)	0.21(S,3H,SiMe), 0.22(S,3H,SiMe), 1.85(m,4H,3.4-CH$_2$), 3.38(m,1H,2-CH), 3.75(m,2H,5-CH$_2$),	232(M$^+$,5), 217(3), 189(20), 161(43), 146(15), 145(90), 135(28), 131(20), 130(100), 129(22),

Table 2 (continued)

Hydrosilane	Alkene or alkyne	Hydrosilylation products (yield,%)	^{1}H NMR (δ,ppm; J,Hz)	MS, m/e (rel.intensity, %)
			6.45(d,1H,J=19.4, a-H), 6.99(d,1H, J=19.4, b-H), 7.2-7.5(m,5H,Ph)	128(68), 113(16), 89(10), 75(60), 59(64)
II	PhC≡CH	 (25)	0.18(S,3H,SiMe), 0.24(S,3H,SiMe), 1.85(m,4H,3.4-CH_2), 3.38(m,1H,2-CH), 3.75(m,2H,5-CH_2), 5.70(d,1H,J=2.9,C=CH), 5.92(d,1H,J=2.9,C=CH), 7.2-7.5(m,5H,Ph)	232(M^+,1.3), 217(3), 204(81), 203(16), 189(44), 161(26), 145(34), 135(98), 130(100), 101(99), 75(97), 59(53)

To examine the possible application of I and II as reagents for the introduction of di- and tetrahydrofurylsilyl groups their reactions with styrene and phenylacetylene have been studied. The hydrosilylation of these compounds by I and II (100°C, catalyst $H_2PtCl_6 \cdot 6H_2O$, 5-30 min) leads to α- and β-adducts with high yield. In the case of alkynes only the corresponding trans-alkenes are formed (Table 2).

REFERENCES AND NOTES

1. 2-(4,5-Dihydrofuryl)trimethylsilane has been prepared by the reaction between 2-(4,5-dihydrofuryl)lithium and trimethylchlorosilane as described in 2 .
2. F. T. Oakes and J. F. Sebastian. J. Org. Chem., 1980, 45, 4959.
3. Bp, n_D and ^{1}H NMR spectral data of V are in compliance with those described in 4 . Mass-spectrum of V, m/e (rel.intensity, %): 130(M^+, 12), 116(15), 115(100), 87(71), 75(13), 61(17), 59(19).
4. C. L. Smith and R. Gooden. J. Organomet. Chem., 1974, 81, 33.

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