SYNTHESIS OF NOVEL n-ALKTRIENYLTRICHLOROSILANE – VERSATILE REAGENT AND PRECURSOR FOR ORGANIC MONOLAYER FORMATION

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Preparation of (*Z*,*Z*,*Z*)-9,12,15-octadecatrienyltrichlorosilane (**2**) by the reaction of the corresponding Grignard reagent with $SiCl_4$ is described. The novel compound of the type $RSiX_3$, useful for various organometallic applications and with the ability to form close-packed ordered monolayers chemically bonded to the surface, was thoroughly characterized by spectral analysis.

Key words: n-Alktrienyltrichlorosilane; (*Z*,*Z*,*Z*)-9,12,15-Octadecatrienyltrichlorosilane.

Since the synthesis[1] of prototype compound of the general formula $RSiX_3$ (X = Cl, Br, I, F; R = alkyl group having from 1 to 31 C atoms), there has been significant interest for these compounds because of their widespread use in several diverse areas: (i) Selective homogeneous catalysts for hydrogenation and hydroformylation of olefins were prepared[2] from the compounds of that type with $Rh(acac)(CO_2)$ or $RhCl(PPh_3)_3$. (ii) The catalysts, so formed, containing a SiX_3 group, whereby X is a hydrolyzable group, such as Cl, OC_2H_5, NH_2 or OCOR, can be transformed into the supported transition metal complexes[3] by bonding to the silica surface. (iii) The possibility of the monolayer formation at a liquid–solid interface via spontaneous adsorption of active silane molecules on hydroxylated surfaces as glass, quartz, silicon or gold, represents particularly interesting application of the trichlorosilane derivatives[4,5].

For purposes related to above, we required previously unknown $RSiCl_3$ derivative[6] possessing (*Z*,*Z*,*Z*)-9,12,15-octadecatrienyl group as a long unsaturated hydrocarbon chain.

The general approach to the synthesis of this silane (**2**) is illustrated in Scheme 1.

Hydride reduction of methyl linoleate and subsequent reaction with $(n\text{-}C_4H_9)_3P$ in CCl_4 gave by standard procedure[7] the unsaturated chloride (85%). Its conversion to Grignard reagent **1** in the presence of 10% molar excess of Mg, initiated by minute quantity of $BrCH_2CH_2Br$, was accomplished in boiling $THF–C_6H_5CH_3$ mixture in high yield (ca 80%). The addition of Grignard reagent to twofold excess of $SiCl_4$ resulted in formation of (*Z*,*Z*,*Z*)-9,12,15-octadecatrienyltrichlorosilane (**2**) (62% of pure isolated compound based on the unsaturated chloride). In the absence of the substantial excess of $SiCl_4$ compared to RMgCl appreciable amounts of di- and some tri- and tetra-n-alktrienylsilane derivatives were detected (the molar ratio of $SiCl_4$ to RMgCl must be well above 1.5 : 1). Satisfactory microanalytical data have been obtained for this highly air unstable, colorless liquid silane **2**. Its structure was confirmed by spectroscopic analysis. Mass spectrum exhibits molecular ion and the complete sequence of ions $Cl_3Si(CH_2)_x$ (x = 0, 1–8) indicating stepwise loss of CH_2 groups. The IR spectrum shows absorption bands at 3 012, 1 645 and 692 cm^{-1} expected for (*Z*)-CH=CH. Bonds arising[8,9] from –CH=CH–CH_2–CH=CH– fragment at 1 397 cm^{-1} and Si–C at 766 cm^{-1} are also observed. The ^1H NMR and ^{13}C NMR spectra supporting[10,11] the structure of the silane **2** are given in Table I. Particularly instructive data were obtained from ^{13}C NMR spectrum showing identifiable resonances for all 18 C atoms.

Specific application of the compound **2** was directed toward synthesis of the saturated tritiated silane via catalytic hydrogenation with tritium, which then served in a form of mononuclear film absorbed on hydroxylated surface as a thin, uniform and stable source of reasonable intensity for the electron antineutrino mass determination[6].

EXPERIMENTAL

A 100 ml three-necked flask fitted with a rubber septum, magnetic stirrer, condenser and pressure-equalizing addition funnel, was charged with magnesium turnings (0.407 g, 16.9 mmol) in dry THF (5 ml). Maintaining a dry nitrogen atmosphere through an inlet adapter, 6 ml of the solution from the total THF–$C_6H_5CH_3$ mixture 1 : 1 v/v (30 ml) containing (*Z*,*Z*,*Z*)-9,12,15-octadecatrienyl chloride (4.384, 15.4 mmoles) was added at room temperature. The reaction mixture was warmed up to about 60 °C, and then several drops of ethylene dibromide were added to initiate the reaction. The remainder of the alktrienyl chloride solution was added over 1 h to the stirred mixture at a rate maintaining a gentle reflux. The reaction mixture was refluxed for an additional hour with stirring until most of the magnesium was consumed. During the reaction course the aliquots of the reaction mixture withdrawn at regular intervals were quenched with water, and the yield of Grignard reagent (ca 80%) was determined by GLC analysis (which showed two peaks assigned to the unreacted halide and (*Z*,*Z*,*Z*)-9,12,15-octadecatriene). The Grignard solution was transferred via double tip syringe needle to the

$$RCO_2CH_3 \xrightarrow{a,\,b,\,c} \underset{\mathbf{1}}{RCH_2MgCl} \xrightarrow{d} \underset{\mathbf{2}}{RCH_2SiCl_3}$$

$$R = (Z,Z,Z){-}CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_5CH_2{-}$$

a) $LiAlH_4$, ether; b) $(n\text{-}C_4H_9)_3P$, CCl_4;
c) Mg, THF-$C_6H_5CH_3$; d) $SiCl_4$, $C_6H_5CH_3$

SCHEME 1

addition funnel attached to a 3-necked flask that contained twofold excess of $SiCl_4$ (5.236 g, 30.8 mmol) in $C_6H_5CH_3$ (10 ml). The dropwise addition of Grignard reagent over 3 h at 20 °C with gradual formation of $MgCl_2$, was followed by refluxing the reaction mixture for 1 h. The solvent and the resulting silane **2** were separated from $MgCl_2$ by pressure filtration through a filter stick (gas dispersion tube). The fractional distillation under high vacuum yielded 3.71 g (62%) of (*Z*,*Z*,*Z*)-9,12,15-octadecatrienyltrichlorosilane (**2**) (b.p. 135 °C/0.09 Torr). For $C_{18}H_{31}Cl_3Si$ (381.9) calculated: 56.61% C, 8.18% H, 27.85% Cl; found: 56.67% C, 8.40% H, 27.60% Cl.

TABLE I
^1H and ^{13}C NMR data for (*Z*,*Z*,*Z*)-9,12,15-octadecatrienyltrichlorosilane (**2**)

Proton[a]	Chemical shifts[b]	Carbon[c]	Chemical shifts
H–C(18)	0.98 t, 3 H, *J* = 7.6 Hz	C(1)	31.797
H–C(1) to H–C(6)	1.27–1.44 m, 12 H	C(2)	22.296
H–C(7)	1.56 m, 2 H	C(3)	24.375
H–C(8)		C(4)	28.998
allylic	2.06 m, 4 H	C(5)	29.248
H–C(17)		C(6)	29.248
H–C(11)		C(7)	29.618
doubly allylic	2.81 t, 4 H, *J* = 5.6 Hz	C(8)	27.252
H–C(14)		C(9)	130.300
H–C(olefinic)	5.36 m, 6 H	C(10)	127.805
		C(11)	25.682
		C(12)	128.332
		C(13)	123.332
		C(14)	25.587
		C(15)	127.179
		C(16)	132.000
		C(17)	20.586
		C(18)	14.250

[a] ^1H NMR spectrum was recorded at 400 MHz in $CDCl_3$ at room temperature. [b] δ in ppm referred to TMS. [c] ^{13}C NMR spectrum was measured at 150.904 MHz in $CDCl_3$.

REFERENCES

1. Booth H. S., Carnell P. H.: J. Am. Chem. Soc. *68*, 2650 (1946).
2. Allum K. G., Hancock R. D., Howell I. V., McKenzie S., Pitkethly R. C., Robinson P. J.: J. Organomet. Chem. *87*, 203 (1975).
3. Evans D., Yagupski G., Wilkinson G.: J. Chem. Soc., A *1968*, 2660.

4. Sagiv J.: J. Am. Chem. Soc. *102*, 92 (1980).
5. Tillman N., Ulmann A., Schildkraut J. S., Penner T. L.: J. Am. Chem. Soc. *110*, 6136 (1988).
6. Fritschi M., Holzschüh E., Kundig W., Stussi H.: Nucl. Phys. *19*, 205 (1991).
7. Monson R. S.: *Advanced Organic Synthesis, Methods and Techniques*, pp. 18 and 45. Academic Press, New York 1972.
8. Klok R., Mohlmann W. M. M., van der Welf L., Pabon H. J. J.: Rec. Trav. Chim. Pays-Bas *99*, 132 (1980).
9. Ebsworth E. A. V., Onyszchuk M., Sheppard N.: J. Chem. Soc. *1958*, 1453.
10. Gunstone F. D.: Chem. Phys. Lipids *56*, 227 (1990).
11. Gunstone F. D., Pollard M. R., Scrimgeour C. M., Vedanyagam H. S.: Chem. Phys. Lipids *18*, 115 (1977).