Journal of Fluorine Chemistry, 5 (1975) 7 - 11

FLUORO-ORGANOFUNCTIONAL SILICON COMPOUNDS. SYNTHESIS OF ACETOXY, CARBETHOXY AND HYDROXY DERIVATIVES

YUNG K. KIM and OGDEN R. PIERCE

Research Department, Dow Corning Corporation, Midland, Michigan 48640 (U.S.A.)

(Received November 26, 1973)

Summary

The synthesis of fluoro-organosilicon compounds containing acetoxy, carbethoxy, or hydroxy groups in the organic portion of the molecule is described.

Introduction

Although numerous organosilicon compounds having functional groups in the organic portion of the molecule have been reported [1], fluoro-organofunctional silicon compounds are little known. Since many fluorocarbon derivatives are unique in their properties, it was of interest to investigate the preparation and properties of fluoro-organofunctional silicon compounds. In this paper, a number of examples of this class of compounds having an acetoxy, carbethoxy, or hydroxy group in the organic portion of the molecule is described.

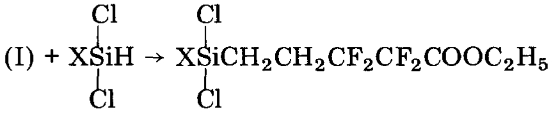
Results and discussion

We have previously reported the preparation of ethyl 3-(vinyl)perfluoropropionate (I) [2]. The lithium aluminum hydride reduction of this ester (I) gave the expected 2,2,3,3-tetrafluoro-3-(vinyl)propanol (II) in good yield. In order to protect the alcoholic function during reaction of the olefinic moiety the alcohol (II) was converted to the corresponding acetate (III). Although some fluoro-olefins are known to undergo allylic displacement reactions with lithium aluminum hydride [3], such a displacement was not apparent to a significant extent in the reduction of ester (I).

$$\underset{\text{(I)}}{H_2C{=}CHCF_2CF_2COOC_2H_5} \xrightarrow{LiAlH_4} \underset{\text{(II)}}{H_2C{=}CHCF_2CF_2CH_2OH} \xrightarrow[(-HCl)]{CH_3COCl}$$

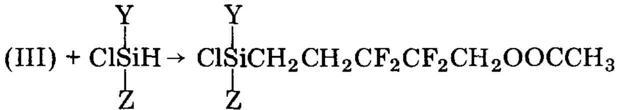
$$\underset{\text{(III)}}{H_2C{=}CHCF_2CF_2CH_2OOCCH_3}$$

The chloroplatinic acid catalyzed addition of the ≡SiH moiety to esters (I) and (III) proceeded smoothly to yield the corresponding functional fluorosilanes (IV) and (V), respectively.



$$\text{(I)} + \text{X}\underset{\text{Cl}}{\overset{\text{Cl}}{\text{Si}}}\text{H} \rightarrow \text{X}\underset{\text{Cl}}{\overset{\text{Cl}}{\text{Si}}}\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{COOC}_2\text{H}_5$$

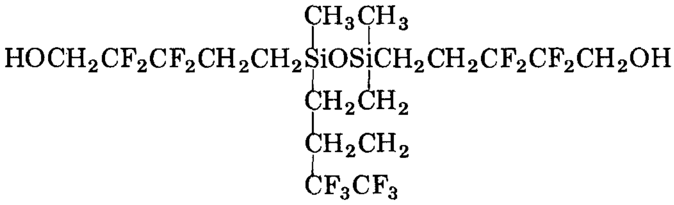
(IV)(a): $X = CH_3$
(b): $X = Cl$



$$\text{(III)} + \text{Cl}\underset{\text{Z}}{\overset{\text{Y}}{\text{Si}}}\text{H} \rightarrow \text{Cl}\underset{\text{Z}}{\overset{\text{Y}}{\text{Si}}}\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{OOCCH}_3$$

(V)(a): $Y = CH_3$, $Z = CF_3CH_2CH_2$
(b): $Y = Cl$, $Z = CH_3$
(c): $Y = Z = Cl$

The reaction of silane (V)(a) with an excess of methanol at reflux temperature followed by the fractional distillation of the mixture resulted in the formation of disiloxane (VI) in good yield.



$$\text{HOCH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\underset{\substack{\text{CH}_2\\ \text{CH}_2\\ \text{CF}_3}}{\overset{\text{CH}_3}{\text{Si}}}\text{O}\underset{\substack{\text{CH}_2\\ \text{CH}_2\\ \text{CF}_3}}{\overset{\text{CH}_3}{\text{Si}}}\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}$$

(VI)

Experimental

All boiling points are uncorrected. The ^{19}F NMR spectra were measured on a Varian T-60 NMR spectrometer operating at 56.4 MHz. Chemical shifts were determined in ppm using CCl_3F as an internal standard. The proton resonance spectra were obtained on a Varian A-60 NMR spectrometer using tetramethylsilane as an internal standard. Infrared absorption spectra were determined on a Perkin–Elmer Model 137 Infracord.

2,2,3,3-Tetrafluoro-3-(vinyl)propanol (II)

Into a stirred mixture consisting of 20 g (0.53 mol) of lithium aluminum hydride and 400 cm^3 of dry ether was added dropwise 100 g (0.50 mol) of ethyl 3-(vinyl)perfluoropropionate at 0 - 5 °C under an atmosphere of nitrogen. After the addition was complete, the reaction mixture was heated under reflux for 3.5 h. The excess lithium aluminum hydride was decomposed by the dropwise addition of water (*ca.* 100 cm^3) at 0 - 5 °C. The reaction mixture was then acidified with hydrochloric acid and poured into ice-cold water. The ether layer was separated and dried over Drierite. After evaporation of the ether, the resulting product was distilled to yield 69 g (87% yield) of (II), b.p. 135 °C, n_D^{25} 1.3605.

Analysis: Found: C, 38.2; H, 3.80%. $C_5H_6F_4O$ requires C, 37.97; H, 3.80%

The ^{19}F resonance spectrum consisted of signals centered at +115.3 ppm and +124.0 ppm with an area ratio of one to one.

2,2,3,3-Tetrafluoro-3-(vinyl)propyl acetate (III)

Into a stirred solution consisting of 100 g (0.634 mol) of 2,2,3,3-tetrafluoro-3-(vinyl)propanol (II) and 77 g (0.762 mol) of triethylamine in 300 cm^3 of dry ether was added dropwise 60 g (0.764 mol) of acetyl chloride at 0 - 5 °C. After the addition was complete, the reaction mixture was heated under a mild reflux for several hours with stirring. The salt was removed by filtration and the filtrate was distilled to yield 110 g (88% yield) of (III), b.p. 62 °C (18 mmHg), n_D^{25} 1.3650.

Analysis: Found: C, 42.4; H, 4.14; F, 37.4%. $C_7H_8F_4O_2$ requires C, 42.01; H, 4.03; F, 37.97%.

The ^{19}F resonance spectrum exhibited signals centered at +115.8 ppm and +122.1 ppm. The relative areas were equivalent.

Addition of ≡SiH to functional fluoro-olefins

The preparation of ethyl 2,2,3,3-tetrafluoro-5-(methyldichlorosilyl)-pentanoate, (IV)(a), is described as a typical example of the procedure. The results of other preparations are summarized in Table 1.

Into a stirred mixture of 150 g (0.75 mol) of ethyl 3-(vinyl)perfluoropropionate (I) and 0.75 cm^3 of a 0.1 mol l^{-1} solution of chloroplatinic acid in ethanol was added dropwise 92 g (0.80 mol) of methyldichlorosilane at 110 - 120 °C under an atmosphere of nitrogen. After completion of the addition, the reaction mixture was kept at room temperature overnight. Distillation of the reaction mixture gave 22 g (14% recovery) of (I) and 183 g (89% yield) of (IV)(a), b.p. 120 - 121 °C (20 mmHg), n_D^{25} 1.4065.

Analysis: Found: C, 30.5; H, 3.81; F, 24.1; Si, 8.47%. $C_8H_{12}Cl_2F_4O_2Si$ requires C, 30.49; H, 3.84; F, 24.11; Si, 8.91%.

The spectral properties were in agreement with the assigned structure (IV)(a), the ^{19}F resonance spectrum consisting of signals centered at +116.8 ppm and +120.2 ppm with an area ratio of 1:1.

Preparation of the disiloxane (VI)

A solution consisting of 10 g (0.026 mol) of silane (V)(a) in 15 cm^3 of methanol was heated under reflux for 2 h. Distillation of the reaction mixture gave 6.2 g (72.3%yield) of (VI), b.p. 225 °C (0.5 mmHg), n_D^{25} 1.3925.

Analysis: Found: C, 35.28; H, 4.61%. $C_{18}H_{28}F_{14}O_3Si_2$ requires C, 35.18; H, 4.59%.

The ^{19}F resonance spectrum exhibited signals centered at + 69.1 ppm (3F), +118.0 ppm (2F) and +124.0 ppm (2F). The infrared and proton resonance spectra were also consistent with structure (VI).

TABLE 1

Fluoro-organofunctional silicon compounds

Product	B.p./°C (mmHg)	n_D^{25}	Yield (%)	Formula	Analysis									
					Calculated (%)					Found (%)				
					C	H	Cl	F	Si	C	H	Cl	F	Si
(IV)(a)	120 - 121 (20)	1.4065	89	$C_8H_{12}Cl_2F_4O_2Si$	30.49	3.84		24.11	8.91	30.5	3.81		24.1	8.47
(IV)(b)	98(6)	1.4080	72	$C_7H_9Cl_3F_4O_2Si$	25.05	2.71		22.64	8.37	25.7	2.95		22.8	8.51
(V)(a)	94(0.25)	1.3925	63	$C_{11}H_{16}ClF_7O_2Si$	35.06	4.28	9.41			35.34	4.38	8.92		
(V)(b)	91(1.5)	1.4105	41	$C_8H_{12}Cl_2F_4O_2Si$	30.49	3.84	22.5	24.11		30.68	3.92	22.4	24.6	
(V)(c)	92(0.75)	1.4130	88	$C_7H_9Cl_3F_4O_2Si$	25.07	2.70	31.70			25.05	2.75	31.71		

Acknowledgements

The authors wish to thank Mr. J. C. Lavis for his technical assistance.

References

1 J. L. Speier in R. E. Kirk and D. F. Othmer (Eds.), Organofunctional Silicon Compounds, Encyclopedia of Chemical Technology, Vol. 14, Wiley-Interscience, New York, 1967, pp. 755 - 770.

2 Y. K. Kim and O. R. Pierce, J. Org. Chem., 34 (1969) 602.

3 (a) G. Fuller and J. C. Tatlow, J. Chem. Soc., (1961) 3198.
(b) D. E. M. Evans *et al.*, J. Chem. Soc., (1963) 4828.
(c) M. H. Kaufman *et al.*, J. Org. Chem., 32 (1967) 2749.