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PREPARATION OF SOME CYCLIC FLUOROSILANES

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SUMMARY

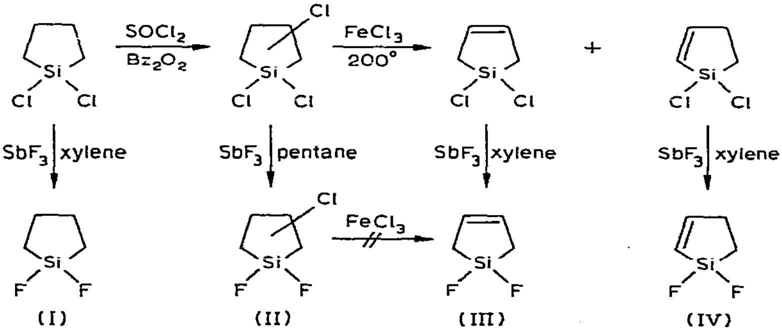
Fluorination with SbF_3 has been used to prepare 1,1-difluoro-1-silacyclopent-3-ene, 1,1-difluoro-1-silacyclopent-2-ene, 1,1-difluoro-1-silacyclopentane and a mixture of 1,1-difluoro-2-chloro-1-silacyclopentane and its 3-chloro isomer from the appropriate chlorosilanes. IR and NMR spectra of the products are reported.

RESULTS

The preparation of several five-membered ring fluorosilanes has been achieved in good yield by reacting the appropriate chlorosilanes with antimony trifluoride. This method for preparing fluorosilanes is well-established[1,2] but in certain reactions ring cleavage can result when SbF_3 is used[3]. It was therefore a concern in this study whether the five-membered rings of interest would be cleaved by SbF_3. Furthermore, it was not clear whether the double-bonds present in two of the molecules would react with the reagent. A preliminary test during which SbF_3 was heated with cyclohexene for several hours suggested that the double bonds would probably not react.

The reaction scheme employed is shown in Scheme 1. 1,1-Difluoro-1-silacyclopentane (I), 1,1-difluoro-1-silacyclopent-3-ene (III), 1,1-difluoro-1-silacyclopent-2-ene (IV), and a mixture (II) of 1,1-difluoro-2-chloro-1-silacyclopentane and 1,1-difluoro-3-chloro-1-silacyclopentane were prepared from the analogous dichloro compounds. All compounds were obtained in good yield and the formation of no side-products was observed. Apparently no ring cleavage or reaction with double bonds occurred.

SCHEME 1



The difluorosilacyclopentenes [(III) and (IV)] could not be obtained from the monochlorinated difluorosilacyclopentane (II) by heating it with catalytic quantities of ferric chloride. The relatively low boiling point (109°) of the difluoro ring compound apparently makes it impossible for the necessary reaction temperature to be achieved. The analogous dichloro compound begins to eliminate HCl at about 160°.

Spectral data

Table 1 lists the NMR τ values for the hydride, fluoride, and chloride derivatives of four different types of ring systems. For the five-membered rings the values for analogous proton peaks are for the most part very little changed from one derivative to another. Only the hydrogens on the carbon α to the silicon show a noticeable shift to lower τ values when Cl replaces either F or H.

Table 2 lists the infrared frequencies which were found to be relatively constant for a particular type of ring system and which had at least moderate intensity. These can be considered as characteristic of that particular ring structure. The bands in the 900–1650 cm^{-1} region are especially useful for identifying the ring framework.

The NMR and infrared data in Tables 1 and 2 should make it a simple task to confirm with reasonable certainty whether a newly prepared derivative has one of these ring structures.

TABLE 1

NMR DATA FOR CYCLIC SILANES (τ VALUES)

Compound	Proton	Chemical shift, X=			Description (for fluoride)
		H	F	Cl[a]	
$CH_2CH_2\overset{2}{CH_2}\overset{1}{CH_2}SiX_2$	1	9.22	9.33	8.89	Multiplet (11 peaks)
	2	8.41	8.32	8.22	Multiplet (9 peaks)
	H(Si)	6.17			
$CH_2\overset{2}{CH}=CH\overset{1}{CH_2}SiX_2$	1	8.62	8.67	8.18	Triplet of doublets
	2	4.20	4.06	4.05	Triplet of triplets
	H(Si)	6.13			
$\overset{4}{CH_2}\overset{3}{CH_2}\overset{2}{CH}=\overset{1}{CH}SiX_2$	1	4.10	4.12	3.88	Doublet of quintets
	2	3.15	2.65	2.88	Multiplet (11 peaks)
	3	7.40	7.55	7.36	Multiplet (13 peaks)
	4	9.02	9.25	8.73	Multiplet (8 peaks)
	H(Si)	5.80			
$CH_2\overset{2}{CH_2}\overset{1}{CH_2}SiX_2$[b]	1	8.9	8.3	7.9	Overlapping Multiplet
	2	7.7	8.3	7.9	
	H(Si)	5.3			

[a] Data for chlorides from ref. 5. [b] Data for silacyclobutanes from ref. 3.

TABLE 2

CHARACTERISTIC INFRARED BANDS FOR CYCLIC SILANES (±5 CM^{-1})

Compound	X	IR frequencies									
$CH_2CH_2CH_2CH_2SiX_2$	H	2950	2870	1460	1420	1250	1080	1040	890	840	760
	D[a]	2950	2870	1460	1420	1250	1080	1030	860	810	710
	F	2950	2890	1470	1430	1270	1090	1040	890	800	710
	Cl	2940	2880	1450	1400	1250	1080	1030	850	800	730, 710
$CH_2CH{=}CHCH_2SiX_2$	H	3040	2930	1620	1400	1210	1110	960	730	670	
	D	3040	2930	1620	1410	1210	1110	940	720	670	
	F	3040	2930	1610	1400	1210	1110	940	780	650	
	Cl	3040	2900	1610	1400	1210	1110	950	730	640	
$CH_2CH_2CH{=}CHSiX_2$	H[b]	2990	2900	1560	1440	1320	1140	1100	990	870	700
	F	3020	2940	1570	1440	1320	1160	1100	990	840	710
	Cl	3020	2930	1560	1440	1320	1150	1100	990	830	760

[a] Data from ref. 7. [b] Data from ref. 5.

EXPERIMENTAL

Materials

Commercially available xylene was dried over magnesium sulfate and distilled prior to use. Antimony trifluoride was purchased from Baker & Adamson Products and used without further purification.

Preparation of compounds

Since all of the hydrides and halides of silicon dealt with are hydrolyzed by water, it was necessary to use a steady stream of dried nitrogen to flush the reaction apparatus in each experiment. In most cases a three-necked flask equipped with a dropping funnel, reflux condenser, and a mechanical stirrer was used.

(*A*). *Silanes and chlorosilanes.* 1,1-Dichloro-1-silacyclopentane[4], monochlorinated 1,1-dichloro-1-silacyclopentane[5], 1,1-dichloro-1-silacyclopent-3-ene[5], and 1,1-dichloro-1-silacylopent-2-ene[5] were prepared as described previously. The latter two compounds were separated using a teflon spinning band column[6]. The preparations of silacyclopent-3-ene, silacyclopent-2-ene, and the analogous deuterides have been described earlier[5-7].

(*B*). 1,1-*Difluoro*-1-*silacyclopentane.* 1,1-Dichloro-1-silacyclopentane (82.0 g, 0.53 mole) was dissolved in 80 ml of xylene and the mixture was added dropwise to 75 g (0.42 mole) of antimony trifluoride in 200 ml of xylene. The reaction flask was kept near 0° by an ice bath and rapid stirring was used. Following the addition, which was completed in about 45 min, the ice-bath was removed and the mixture was stirred for two more hours. At this point all the solid had dissolved and the solution had taken on a faint yellow color. The crude product was obtained by distillation through a short vigreux column. This was then redistilled using a teflon spinning-band column to obtain the pure product, b.p. 67°. Yield: 57.9 g (0.48 mole), 89%. (Found: C, 39.04; H, 6.72; F, 31.38. $C_4H_8F_2Si$ calcd.: C, 39.32; H, 6.60; F, 31.10%.)

(*C*). 1,1-*Difluoro*-1-*silacyclopent*-3-*ene.* The procedure used was similar to that in the previous reaction. 25.0 g (0.15 mole) of 1,1-dichloro-1-silacyclopent-3-ene dissolved in 30 ml of xylene was reacted with 19.7 g (0.11 mole) of SbF_3 in 50 ml of xylene. Distillation gave the product (14.0 g, 0.12 mole, 71% yield) boiling at 63°. (Found: C, 39.78; H, 5.01; F, 31.61. $C_4H_6F_2Si$ calcd.: C, 39.98; H, 5.03; F, 31.62%.)

(*D*). 1,1-*Difluoro*-1-*silacyclopent*-2-*ene*. In analogous manner to the previous reactions 1,1-dichloro-1-silacyclopent-2-ene (22.0 g, 0.14 mole) in 20 ml of xylene was added to 19.1 g (0.11 mole) of antimony trifluoride in 75 ml of xylene. Distillation gave 11.1 g (0.092 moles, 65% yield) of product, b.p. 63°. (Found: C, 40.03; H, 5.16; F, 31.73. $C_4H_6F_2Si$ calcd.: C, 39.98; H, 5.03; F, 31.62%.)

(*E*). *Monochlorinated* 1,1-*difluoro*-1-*silacyclopentane*. Monochlorinated 1,1-dichloro-1-silacyclopentane (110.0 g; 0.58 mole) (80% β, 20% α)[5] in 125 ml of pentane was added dropwise to 69.0 g (0.46 mole) of SbF_3 in 200 ml of pentane. Following the reaction the pentane solution was decanted into a distillation flask and the residue was washed with additional pentane which was added to the flask. After removal of the lower boiling pentane, distillation gave 57.1 g (0.36 mole, 62% yield) of the product, b.p. 106–109°. (Found: C, 30.55; H, 4.62. $C_4H_7ClF_2Si$ calcd.: C, 30.68; H, 4.51%.)

Attempted reaction of monochlorinated 1,1-*difluoro*-1-*silacyclopentane with* $FeCl_3$

A mixture of 48.3 g of monochlorinated 1,1-difluoro-1-silacyclopentane (II) and 0.2 g of ferric chloride was refluxed for 24 h but no evolution of HCl occurred. The low boiling point (109°) of the fluoro compound made it impossible to reach the temperature at which gas evolution would begin (~160° for the analogous chloro compound).

Analyses

Analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Spectral measurements

Infrared spectra of liquid samples were obtained using a Beckman IR-12 instrument. NMR data of pure liquids were recorded on a Varian A-60 spectrometer using tetramethylsilane as an internal standard.

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