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Reaction of Vinyl Chloride with Difluorosilylene by Cocondensation

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Abstract: The reaction between difluorosilylene and vinyl chloride by cocondensation at -196°C is studied. Formation of the products is viewed as the result of either ring closure or H migration of a diradical intermediate. The ring-closure process results in two isomers of 4,5-dichloro-1,1,2,2-tetrafluoro-1,2-disilacyclohexane, which are characterized by an analysis of their fluxional behaviors in the ^{19}F NMR spectra. The activation parameter of the cis isomer is obtained and compared with related systems. Relevance of the results of this reaction to an integrated reaction mechanism of insertion vs. addition of oligomeric difluorosilylenes is discussed.

Unlike the well-studied addition reactions with alkynes,¹⁻³ the study of the addition reaction of difluorosilylene with alkenes has been very limited. Ever since Margrave et al.⁴ published their communication on the reaction of difluorosilylene with ethylene, there has been no further work concerning this aspect in the literature in some 12 years. A part of the reason is due to the difficulty in isolating the stereoisomers of the presumably silacyclic products and to the broadened NMR spectra of the products (both ^1H and ^{19}F NMR) which hamper a definite structural characterization of such compounds.^{4,5}

We now report the result of the reaction of difluorosilylenes with vinyl chloride which includes, in our view, the well-characterized 1,2-disilacyclohexane derivatives that leave no doubt about the type of structure that Margrave proposed in his first communication.⁴

Experimental Section

A greaseless vacuum system was used for the reaction and for the manipulation of volatile compounds. SiF_2 was prepared and reacted with vinyl chloride in the same manner as has been described previously.⁶ All gas reagents were products of Matheson Gas Co. used without further purification.

After the reaction, excess SiF_4 and unreacted vinyl chloride were removed completely from the reaction product mixture by pumping through a trap kept at -64°C . (In fact, all reaction products are not

volatile at -45°C so there was no loss of any reaction product by this procedure.) After careful fractionation and fractional sublimation under vacuum, three major products were obtained (designated as I, II, and III). Compound III, a colorless crystal of mp $93-94^\circ\text{C}$,⁷ could be isolated easily because it was not volatile at room temperature. The mixture of compound I and compound II was gently heated (about 40°C) from the bottom of a vertical column in which compound II, a colorless, crystalline material of mp $37-38^\circ\text{C}$, was fractionally sublimed upward while compound I, a colorless liquid, dripped down. The crystalline product collected at the top of the column was II in pure form. However, the liquid left over was found to be a mixture of I and II and remained as it was after all our purification attempts failed. The total yield of the reaction products based on the quantity of vinyl chloride used was estimated to be 25%, exceptionally high for SiF_2 reactions.² The relative yields of these three compounds are approximately 10% for I, 50% for II, and 40% for III. The results of elemental analysis are listed in Table I.

^1H , ^{19}F , and ^{13}C NMR spectra were recorded on a JEOL JNM-60HL and a JEOL FX-100 spectrometer operating at 60/56.4 and 25.1 MHz, respectively. IR and mass spectra were obtained from a Perkin-Elmer 580 IR and a JEOL JMS-100 mass spectrometer. The spectral data are summarized in Tables I and II.

Results and Discussion

The mass spectra of the three compounds show the same molecular formula, $\text{C}_4\text{H}_6\text{Cl}_2\text{Si}_2\text{F}_4$. Chlorine isotope patterns

Table I. IR and Elemental Analysis Data

compd	IR				elemental anal.			
					C	H	Cl	
III	2960 (w),	2920 (w),	1397 (m),	1325 (m),	calcd	18.67	2.33	27.62
	1190 (m),	1160 (m),	1120 (s),	965 (m),				
	925 (s),	880 (s),	855 (m),	790 (s),				
	750 (s),	725 (m)						
II	2960 (w),	2910 (w),	1392 (m),	1330 (w),				
	1305 (w),	1205 (m),	1190 (s),	1167 (m),				
	1150 (s),	1089 (m),	1060 (m),	975 (sh),				
	925 (vs),	895 (vs),	850 (vs),	785 (s),				
	745 (s)							
I + II	2960 (w),	2910 (w),	1575 (m),	1390 (m),	calcd	18.67	2.33	27.62
	1330 (m),	1265 (w),	1190 (m),	1160 (m),	found	18.81	2.54	27.82
	1100 (br),	970 (sh),	925 (s),	850 (s),				
	785 (s),	745 (m)						

Table II. Mass Spectral Data of the Products from the Reaction with Vinyl Chloride

<i>m/e</i>	assignments	I + II	II	III
256	(C ₂ H ₃ Cl) ₂ Si ₂ F ₄ ⁺	2		
221	(C ₂ H ₃) ₂ ClSi ₂ F ₄ ⁺	6	5	6
194	C ₂ H ₃ ClSi ₂ F ₄ ⁺	6	6	8
186	(C ₂ H ₃) ₂ Si ₂ F ₄ ⁺	5	4	2
174	C ₂ H ₂ ClSi ₂ F ₃ ⁺	8		
167	Si ₂ F ₄ Cl	6	8	8
155	(C ₂ H ₃) ₂ ClSiF ₂ ⁺	70	59	68
139	(C ₂ H ₃) ₂ SiF ₃ ⁺ or C ₂ H ₂ Si ₂ F ₃ ⁺	60	29	19
129	C ₂ H ₄ ClSiF ₂ ⁺	34	20	6
128	C ₂ H ₃ ClSiF ₂ ⁺	33	10	6
119	C ₄ H ₅ SiF ₂ ⁺	100	100	100
112	C ₂ H ₃ SiF ₃ ⁺	44		
109	C ₂ H ₃ ClSiF ⁺	23	20	20
105	C ₃ H ₃ SiF ₂ ⁺	6	9	8
101	(C ₂ H ₃) ₂ SiF ⁺	7	33	6
100	C ₄ H ₅ SiF ⁺	6	8	5
94	C ₂ H ₄ SiF ₂ ⁺	9	7	3
93	C ₂ H ₃ SiF ₂ ⁺	42	19	30
85	SiF ₃ ⁺	5		
75	C ₂ H ₄ SiF ⁺	4	3	3
54	C ₄ H ₆ ⁺	29	31	23
53	C ₄ H ₅ ⁺	14	15	20
29	C ₂ H ₅ ⁺	20	20	20
28	C ₂ H ₄ ⁺	5	8	3
27	C ₂ H ₃ ⁺	8	10	7

fit well with the assignment. Elemental analysis of III is in agreement with this formula. Since compound I is not in pure form its molecular formula from the mass spectrum is merely suggestive. The fact that the elemental analysis of a sample which is a mixture of I and II (approximately 20% of compound I) agrees with the formula C₄H₆Cl₂Si₂F₄ seems to confirm that compound I also has this molecular formula.

The ¹H NMR spectrum of compound I consists of a triplet at δ 3.79 (-CH₂Cl), a multiplet at δ 1.59 (SiF₂-CH₂-), and an AB pattern at δ 6.95 and 6.08 (H_A, H_B) which is typical for trans olefinic protons. The three areas of resonance are of equal intensity. The ¹⁹F NMR spectrum shows two broadened complex peaks with equal intensity (at 135.7 and 136.7 ppm upfield from CCl₃F). The ¹³C NMR spectrum of I shows four peaks at 141.9, 123.7, 38.7, and 21.3 ppm, respectively (Figure 1b). Two lower field peaks are doubtless due to olefinic carbons and the two peaks at higher field are assigned to saturated carbons. Based on the broadness of the peaks caused by the couplings with neighboring fluorine atoms, the four peaks are assigned to C-H_A, C-H_B, -CH₂Cl, and SiF₂-CH₂-, respectively. The gas-phase IR spectrum shows, in addition to ν_{CH}, ν_{CCl}, and ν_{SiF}, a band at 1650 cm⁻¹ which is assigned to ν_{C=C}. All these results indicate that compound I has the structure A,

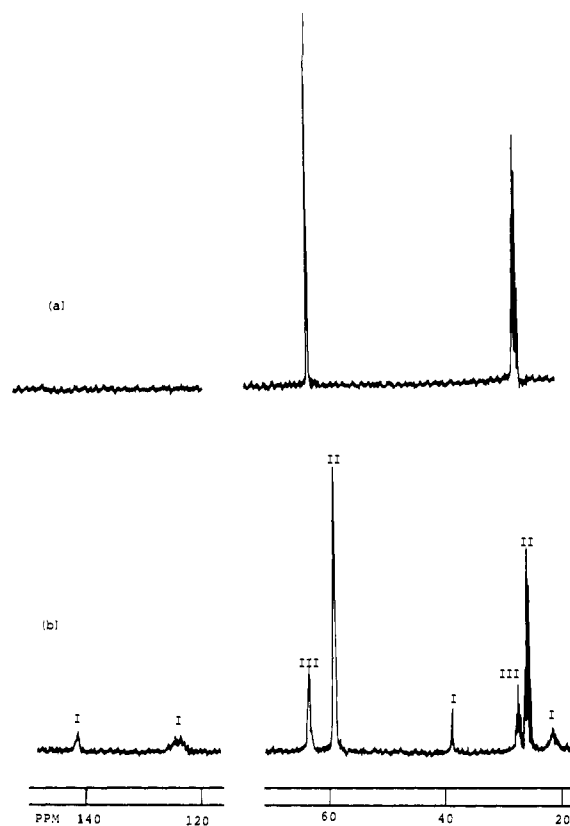
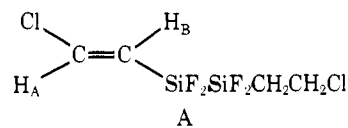
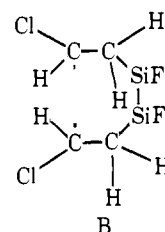


Figure 1. (a) ¹³C NMR spectrum of compound III. (b) ¹³C NMR spectrum of a sample containing I, II, and III.

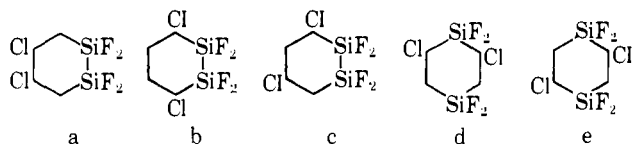


which is formed via a 1,5-H shift in much the same manner as in the reactions of SiF₂ with acetylene and *tert*-butylacetylene.^{1,2} The steric effect of chlorine atom would favor the transition state to assume an orientation with the two olefinic H trans to each other (B).



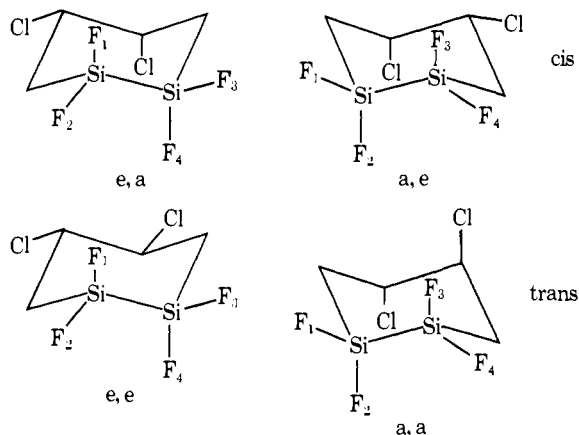
The ^1H NMR spectra of compounds II and III are very similar. Both consist of two broad peaks with intensity ratio 2:1 centering at δ 2.0 and 4.7, respectively. The absence of olefinic protons (IR spectra also show the absence of $\text{C}=\text{C}$ stretching bands) may suggest that compounds II and III are isomers of disilacyclohexanes.

If one assumes that compounds II and III are isomers of disilacyclohexanes, and that vinyl chloride does not undergo any structural change in the reaction, there are five possible structures for the molecular formula $\text{C}_4\text{H}_6\text{Cl}_2\text{Si}_2\text{F}_4$ (a-e).



The ^{13}C NMR spectra of II and III (Figure 1) immediately rule out all structures except (a). This is based on the number of resonance areas and the fact that the carbon peaks at higher field are the peaks with carbon-fluorine couplings.

With the structure of (a), if one assumes that 4,5-dichloro-1,1,2,2-tetrafluoro-1,2-disilacyclohexane has the similar chair-form conformation as in the case of cyclohexane, two isomers are possible—the neighboring chlorine atoms taking cis or trans positions.



While the conformational exchange via ring inversion for the cis isomer would lead to two indistinguishable conformers (e,a and a,e) the two conformers of the trans isomer (e,e and a,a) may exist in equilibrium of different populations.⁸ All four fluorines in either form of the cis isomer are in different chemical environments. When rapid exchange is considered, the four fluorines would exchange in pairs, i.e., $\text{F}_1 \rightleftharpoons \text{F}_3$ and $\text{F}_2 \rightleftharpoons \text{F}_4$, but F_1 would not exchange with F_2 , nor would F_3 with F_4 . In other words, there should be two sets of simultaneous two-site exchange instead of one set of four-site exchange.

This is precisely what was observed in the ^{19}F spectra of compound III. The low-temperature limiting spectrum consists of four separate peaks at 135.2, 136.2, 140.2, and 140.9 ppm, respectively. The peaks at 140.2 and 140.9 ppm appeared as an unresolved peak centered at -140.5 ppm in the spectrum; their chemical shifts are obtained by comparing the centers of weight of the limiting spectra at -80 and 70 °C. The high-temperature limiting spectrum consists of only two peaks (138.6 and 139.3 ppm) of equal intensity. The asymmetrical spectrum at room temperature results from two coalesced peaks, one being more broadened than the other because of the farther separation of the two peaks (135.2 and 140.2 ppm) in the low-temperature limiting spectrum.

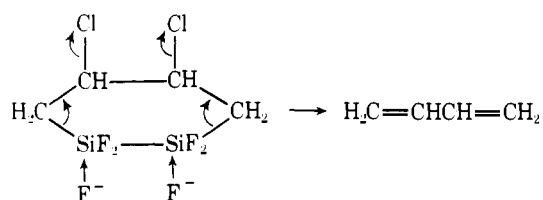
The ^{19}F spectrum of compound II shows two broad and complex peaks at 136.2 and 138.0 ppm. The spectrum does not show any significant change in the temperature range from -80 to 70 °C.

Based on the results described above, we assign compound III to the cis isomer of 4,5-dichloro-1,1,2,2-tetrafluoro-1,2-disilacyclohexane. The fluxional nature of III is the case of exchange of equal populations expected for the cis isomer. Compound II is therefore assigned to the trans isomer. Equilibria of various population ratios of the two conformers of trans 1,2-disubstituted cyclohexanes have been reported;⁹ the complexity seems to arise from a balance of the steric and dipolar interactions of the substituents. The fact that the ^{19}F spectrum of II remains virtually unchanged over a temperature range of -80 to 70 °C seems to indicate that II exists overwhelmingly as one conformer, presumably the (e,e) conformer of the trans isomer.

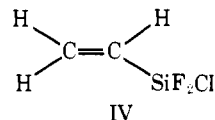
From the spectral change of compound III an activation energy of 11.9 ± 0.2 kcal/mol for ring inversion is obtained. This value is at the upper limit of the known values for 1,2-disubstituted cyclohexane, which range from 10 to 12 kcal/mol.^{10,11} The result is probably more suitably comparable with the case of dithiocyclohexane systems, where the activation parameters range from 11.6 to 13.8 kcal/mol.^{12,13} The presence of two adjacent heteroatoms in the ring would bring about some extra barrier to the inversion of the ring system due to increased bond-angle deformation.

The characterization of compounds I-III seems to agree with the earlier proposed reaction mechanism for alkyne systems, in which the attack of $(\text{SiF}_2)_n$ diradicals on the carbon-carbon multiple bonds leaves a diradical transition state ready for either ring closure or H migration.^{1,2}

One further evidence for the formation of disilacyclohexane came from the result of the hydrolysis of compound III. When III was reacted with 10% aqueous HF solution in a sealed tube, the major product was found to be 1,3-butadiene. The mechanism may be complex; however, one could rationalize the reaction as the result of an initial attack of either fluoride ion or water molecule on the silicon atoms, followed by chlorine elimination.



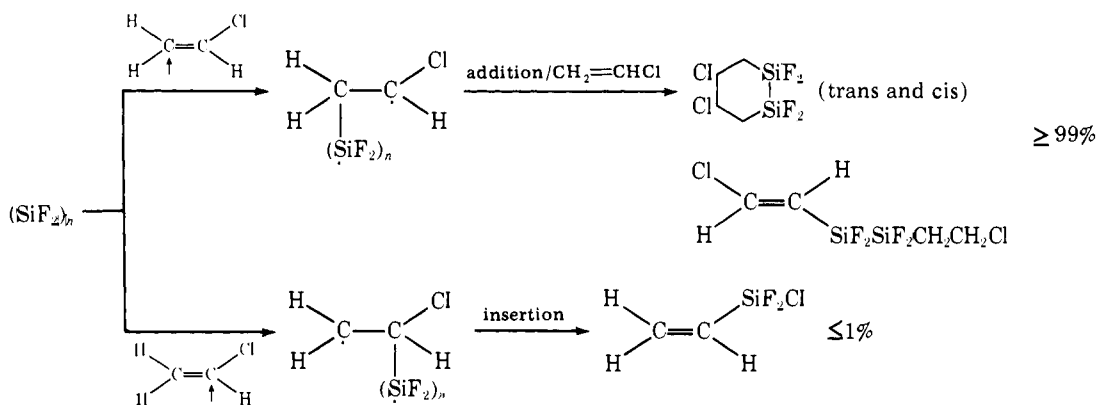
It is worth noting that a small amount (less than 1% of the total reaction products) of "insertion product" is formed in this reaction. The ^1H NMR spectrum of the "insertion" compound shows a complex ABC system at δ 5-6 and no resonance appears in the region for saturated protons. The ^{19}F NMR spectrum shows at 126.9 ppm a doublet of doublets which resembles a triplet because of the nearly equal value of the coupling constants (2.5 Hz for both). These results strongly suggest the existence of an insertion product, vinyldifluorochlorosilane (IV). The ABC pattern at δ 5-6 in the ^1H NMR



is typical for vinyl protons and it is known from previous studies^{14,15} that the trans $J_{\text{H,SiF}}$ and geminal $J_{\text{H,SiF}}$ are of similar magnitude (2-5 Hz), and the cis $J_{\text{H,SiF}}$ is often negligible (≤ 1 Hz).

The existence of IV in this reaction, though in very small quantity, bears mechanistic significance. Up to the present time the only type of insertion reaction of $(\text{SiF}_2)_n$ with olefins that has been reported is the insertion into olefinic C-F bonds.^{16,17} In a recent communication¹⁵ we rationalized this phenomenon with an integrated mechanism in which the insertion reaction

Scheme I



was triggered by the formation of an exceedingly strong Si-F bond (135 kcal/mol vs. 116 kcal/mol for CF)¹⁸ during the reaction. Now we observe the insertion of SiF₂ into an olefinic C-X bond other than C-F, and it is the first time that we observe "addition" and "insertion" products in the same reaction. The difference in bond energies of Si-Cl (91.0 kcal/mol) and C-Cl (78.2 kcal/mol)¹⁸ is less than that of the fluorides; still, 13 kcal/mol of difference is considerably large and one might expect that insertion should prevail after the initial attack of (SiF₂)_n on the carbon-carbon double bond. However, there is one complication in the present case: the result in this work does not necessarily reflect the competitive preference of insertion vs. addition; rather, it may mainly reflect the very large difference in the preference of initial radical attack on the two sides of the double bond that may exist in the case of vinylchloride,^{19,20} (see scheme 1).

In view of this, it is desirable to look at the reaction products from the reactions of (SiF₂)_n with other symmetrically halogen-substituted ethylenes, such as *cis*- and *trans*-dichloroethylene and *cis*- and *trans*-dibromoethylene, where no such preference of initial attack is possible.²¹ Since the difference in bond energies between Si-X and C-X decreases down the halogen group, somewhere along the line one should be able to observe both insertion and addition products from the same reaction which reflect the true competitive preference of insertion vs. addition after the initial attack of oligomeric difluorosilylenes.

Recently Professor Seyferth's group published their elegant work on the synthesis and chemistry of 1,1-difluoro-2,2,3,3-tetramethyl-1-silirane,²² which suggested an alternative to the mechanism of the reaction of SiF₂ with alkenes and alkynes. They suggested that (1) in these reactions siliranes (or silirenes) were formed initially; (2) 1,2-disilacyclobutanes (or 1,2-disilacyclobutenes) were formed by subsequent reactions of siliranes (or silirenes) with SiF₂; (3) all other 2:2 (SiF₂ unit to alkene or alkyne ratio) products were formed through $\dot{\text{C}}\text{CSiF}_2\text{SiF}_2\dot{\text{C}}\text{C}$ diradicals which were formed via radical coupling process of $\dot{\text{C}}\text{CSiF}_2$.

In fact, such an alternative has long been considered and was never excluded from our interpretation of SiF₂ chemistry.^{5,23} However, there are a few points we would like to emphasize: (1) in our view the $\dot{\text{C}}\text{CSiF}_2$ coupling mechanism is probably less favored because one other coupling product, $\text{SiF}_2\text{CCSiF}_2\dot{\text{C}}\text{C}$, would also be expected, yet no evidence has been reported for the existence of any product which might be formed via such diradical intermediates; (2) practically all known SiF₂ chemistry has been done by the cocondensation method at -196 °C, and at this temperature there is rather solid evidence for the existence of paramagnetic, diradical species (SiF₂)_n;²⁴ on the other hand, the reaction of silirane (or silirene) with SiF₂ to give 1,2-disilacyclobutane (or 1,2-disilacyclobutene) is merely hypothetical; (3) the claim by Seyferth that in the case of fluoroethylene reactions with SiF₂

the products could be rationalized unambiguously in terms of silirane intermediates²² is probably at best only relevant to the case of monomeric SiF₂ insertion, for in these reactions there are also products such as FHC=CHSiF₂SiF₃ and FHC=CHSiF₂SiF₂SiF₃¹⁵ whose formation cannot be rationalized by any simple mechanism involving siliranes without raising more skeptical assumptions.

In summary, we feel reluctant to include into the mechanism the intermediate silirane (or silirene) at this time, when no definite evidence for its existence is found under the very special reaction conditions used in our experiments. We fully share Professor Seyferth's view that there is no need to postulate more complex mechanisms in the absence of compelling evidence in their favor when simpler mechanisms are possible.

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