

Short Communication

Reactions of silicon difluoride with unsaturated compounds Part V. Fluoroalkenes

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Introduction

It has been reported that the main products obtained from reactions of silicon difluoride with fluorinated aromatic compounds are those in which insertion of silicon difluoride into carbon-fluorine bonds has occurred with retention of the aromatic ring system¹. This type of product is in marked contrast to that formed from aromatic hydrocarbons where addition to the unsaturated carbon atoms occurs. The same difference was briefly reported to be shown in reactions of silicon difluoride with ethylene derivatives². We report in this paper our studies on a number of fluoro-substituted alkenes, which have resulted in the preparation of a series of vinyl-substituted silicon fluorides.

Results and discussion

Each reaction yielded small amounts of volatile products and a solid involatile residue. The latter ignited violently on contact with laboratory air, and, on a number of occasions, was found to decompose explosively on gentle warming in the vacuum line. These tendencies increased with the number of fluorine atoms in the starting reagent. The volatile products which have been definitely identified are listed in Table 1, with NMR data in Table 2. Mass spectra provided information about the molecular formulae, and the infrared spectra, though similar in each case, showed bands in the region 1600–1650 cm⁻¹, assigned to C=C stretching modes.

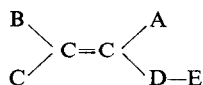
TABLE 1
COMPOUNDS IDENTIFIED FROM SiF₂-FLUOROALKENE REACTIONS

Reagent	Identified compounds
H ₂ C=CHF	H ₂ C=CHSiF ₃ , H ₂ C=CHSiF ₂ SiF ₃
H ₂ C=CF(CH ₃)	H ₂ C=C(CH ₃)SiF ₃ , H ₂ C=C(CH ₃)SiF ₂ SiF ₃
H ₂ C=CF ₂	H ₂ C=CFSiF ₃ , H ₂ C=C(SiF ₃) ₂
F ₂ C=CHF	F ₂ C=CHSiF ₃ , F ₂ C=CHSiF ₂ SiF ₃

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TABLE 2

NMR DATA FOR FLUOROALKENE-SiF₂ PRODUCTS (PROTON CHEMICAL SHIFTS IN τ ; FLUORINE CHEMICAL SHIFTS IN PPM UPFIELD FROM CCl₃F (INTERNAL REFERENCE); COUPLING CONSTANTS IN Hz).



Compound	Chemical shifts					Coupling constants (est.)
	A	B	C	D	E	
H ₂ C=CHSiF ₃	H 3.8	H 3.8	H 3.8	SiF ₃ 140.0	—	Not assigned
H ₂ C=CHSiF ₂ SiF ₃	H 3.8	H 3.8	H 3.8	SiF ₂ 135.4	SiF ₃ 124.2	<i>J</i> (DE) = 14.5
H ₂ C=C(CH ₃)SiF ₃	CH ₃ 8.05	H 4.0	H 4.0	SiF ₃ 143.8	—	<i>J</i> (AD) = 0.5, <i>J</i> (BD) = 3.5
H ₂ C=C(CH ₃)SiF ₂ SiF ₃	CH ₃ 8.10	H 4.0	H 4.0	SiF ₂ 136.4	SiF ₃ 123.1	<i>J</i> (BD) = 3.6, <i>J</i> (DE) = 14.5
H ₂ C=CFSiF ₃	F 114.0	H 4.31	H 4.59	SiF ₃ 140.2	—	<i>J</i> (AB) = 29.5, <i>J</i> (AC) = 56.0 <i>J</i> (AD) = 3.5, <i>J</i> (BD) = 2.5
H ₂ C=C(SiF ₃) ₂	SiF ₃ 137.1	H 3.72	H 3.72	SiF ₃ 137.1	—	Not assigned
F ₂ C=CHSiF ₃	H 6.07	F 49.6	F 55.0	SiF ₃ 137.7	—	<i>J</i> (AB) = 6.0, <i>J</i> (AC) = 37.5 <i>J</i> (AD) = 2.0, <i>J</i> (BC) = 9.0 <i>J</i> (BD) = 12.0, <i>J</i> (CD) = 8.0
F ₂ C=CHSiF ₂ SiF ₃	H 5.95	F 49.8	F 52.3	SiF ₂ 135.8	SiF ₃ 124.1	<i>J</i> (AB) = 6.0, <i>J</i> (AC) = 38.0 <i>J</i> (AD) = 3.0, <i>J</i> (AE) = 0.5 <i>J</i> (BC) = 6.0, <i>J</i> (BD) = 10.0 <i>J</i> (BE) = 1.0, <i>J</i> (CD) = 6.0 <i>J</i> (CE) = 3.0, <i>J</i> (DE) = 16.0

The two compounds obtained from vinyl fluoride had virtually identical and very complex proton NMR spectra. This complexity and small difference in chemical shifts between the three protons in a H₂C=CH- group bound to a silicon fluoride group has been observed previously in H₂C=CHSiF₃³ and in a number of other derivatives⁴. The characteristic triplet-quartet pattern of the Si₂F₅ group observed in the fluorine spectrum of H₂C=CHSiF₂SiF₃ readily distinguishes this compound from H₂C=CHSiF₃ which shows only one complex peak in its fluorine spectrum. Similar observations can be made for the two compounds obtained from 2-fluoropropene, where the fluorine NMR spectra again serve as the main basis for identification.

The compounds obtained from 1,1-difluoroethylene are slightly different in that two isomers are possible for [F₂C=CH₂(SiF₂)₂]. Our assignment of this compound as H₂C=C(SiF₃)₂ is based upon the observation of only one peak in both the proton and fluorine spectra. The alternative isomer H₂C=CF(SiF₂SiF₃) might be expected to show two and three areas of resonance in the proton and fluorine regions respectively. The overall patterns which we find are quite similar

to those reported for $\text{CH}_3\text{CHBrCHBrCH}_3$ ⁵ which would have the analogous $\text{AA}'\text{X}_3\text{X}'_3$ spin system. Our assignment is confirmed by the fact that this compound gives ethylene and not vinyl fluoride (as does $\text{H}_2\text{C}=\text{CFSiF}_3$) on hydrolysis with dilute hydrofluoric acid.

The most complex reaction is that with trifluoroethylene, where there are three possible isomers for the 1:1 product and six for the 1:2 (alkene: SiF_2) product. The NMR spectra of the 1:1 products indicate that one isomer predominates, and, since the main hydrolysis product is 1,1-difluoroethylene, we assign its structure as $\text{F}_2\text{C}=\text{CH}(\text{SiF}_3)$. Various deductions can then be made as to the magnitudes of the spin-coupling constants and chemical shifts in relation to the positions of the atoms in the structure. As a result of this we assign the structure $\text{F}_2\text{C}=\text{CH}(\text{SiF}_2\text{SiF}_3)$ to the most abundant of the 1:2 compounds, which is consistent with it also giving $\text{F}_2\text{C}=\text{CH}_2$ on hydrolysis. The four areas of fluorine resonance for this compound each show very complex coupling patterns but these are assignable in terms of the expected values for the coupling constants. In each of the two mixtures of products we also observe much less intense patterns in the proton spectra based on H-F coupling constants of around 80 Hz, rather than 38 Hz found for the two compounds previously discussed. These we assign to *gem* H-F couplings⁶, and since there are two sets of these patterns in each case we can thus tentatively identify both isomers of $(\text{SiF}_3)\text{FC}=\text{CHF}$, and the corresponding Si_2F_5 derivatives. The fluorine spectra are both too weak and too complex to allow definite assignments, but, since from the mixture of hydrolysis products of the 1:2 products we observe proton and fluorine spectra of vinyl fluoride and *cis*- and *trans*-1,2 difluoroethylene⁷ in addition to 1,1-difluoroethylene, it would appear that both isomers of $(\text{Si}_2\text{F}_5)\text{FC}=\text{CHF}$ and also $(\text{SiF}_3)_2\text{C}=\text{CHF}$ are present in the mixture.

From all of these reactions we also obtain, in very small quantities, mixtures of compounds that are much less volatile and also readily decompose to involatile tars and volatile perfluorosilanes. The common feature of these species is that their proton NMR resonances are in the $\tau = 8$ region associated with protons bound to saturated rather than unsaturated carbon atoms. It is thus likely that these compounds are based on ring structures as is commonly found for non-fluorinated alkenes⁸, but that a ready transfer of fluorine from carbon to silicon occurs leading to the formation of polymers.

The stable products thus result from insertion of SiF_2 or $(\text{SiF}_2)_2$ into a carbon-fluorine bond. It is noteworthy that compounds are formed which contain only one silicon atom, as distinct from those obtained from alkynes⁴ and other alkenes⁸ which show a minimum of two silicon atoms, and which are thought to derive from the $\cdot\text{SiF}_2\text{SiF}_2\cdot$ biradical. A rough consideration of the bond energies involved indicates that the $\text{C}=\text{C}-\text{SiF}$ grouping would be more favourable than $\text{C}-\text{CF}-\text{Si}$, and it may well be this factor rather than any mechanistic differences which determines the nature of the observed products.

Experimental

The fluoroalkenes were available commercially and were checked for purity by comparison of their NMR spectra with published data^{6,9,10}.

Silicon difluoride was prepared and the reactions performed by the previously reported methods¹¹. Approximately equimolar quantities of SiF₂, SiF₄ and fluoroalkene were co-condensed at -196° to give brightly coloured deposits, which evolved volatile material and left brown residues on warming to room temperature. The volatile products were manipulated in a greaseless vacuum line and studied by standard techniques. WARNING: Several violent and potentially serious explosions have occurred either on contact of the residues with air or on warming the residues to 150° in the vacuum line.

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