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REACTIONS OF DIFLUOROSILYLENE WITH CYCLIC ALKENES: CYCLOPENTADIENE AND CYCLOHEPTATRIENE

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Summary

The reactions of difluorosilylene with cyclopentadiene and cycloheptatriene were studied both in the gas phase and by the cocondensation method. Several new organosilicon compounds were synthesized and their structures characterized. In the cycloheptatriene reaction the comparison between the results from the gas phase and cocondensation experiments provides the first solid evidence which makes it possible to differentiate between the silirane mechanism and the $\cdot SiF_2SiF_2 \cdot$ diradical mechanism in the "addition reactions" of difluorosilylene.

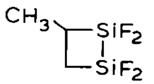
Introduction

The reactions of difluorosilylene with cyclic olefins such as cyclopentene and cyclohexadiene [1] have been reported previously. The results were consistent with the mechanism involving the $\cdot SiF_2SiF_2 \cdot$ diradical intermediate [2,3]; however, the products were equally well explained by the mechanism involving the initial formation of a silirane intermediate [4].

Previous studies on the insertion reactions of difluorosilylene with fluorine-substituted ethylenes [5] have confirmed that monomeric SiF_2 attacks the carbon–carbon double bond, the adduct then rearranges to an insertion product such as $CH_2{=}CHSiF_3$, and the $\cdot(SiF_2)_n\cdot$ ($n = 2, 3$) diradicals are responsible for the formation of $CH_2{=}CH(SiF_2)_nF$ ($n = 2, 3$) in the cocondensation reactions at −196°C.

The strategy used to prove the involvement of the $\cdot SiF_2SiF_2 \cdot$ diradical mechanism is as follows: the selection of one product which can not possibly be formed by dimerization of the silirane intermediate, e.g., $CH_2{=}CHSiF_2SiF_3$ (in the case of the $CH_2{=}CHF/SiF_2$ reaction), only proves that it cannot be formed by sequential insertion of SiF_2 either [5]. In the case of dimethylsilylene, Sakurai et al. have reported the differentiation between the silylene and disilene mechanisms [6].

The attempt to clarify the reaction mechanism in the addition reactions, however, encounters some difficulties. For example, the addition reaction of difluorosilylene with propene under cocondensation conditions yielded the disilacyclobutane **1**, disilacyclohexane **2**, and disilane **3** as products [3,7].



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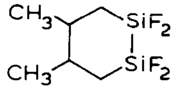

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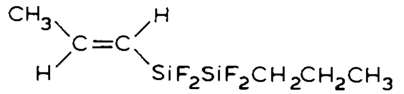


(3)

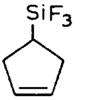
Both the silirane mechanism and the diradical $\cdot SiF_2SiF_2 \cdot$ mechanism have been proposed to account for these products [3,7]. In this case compound **1** can not possibly be formed by dimerization of the silirane intermediate. However, the formation of **1** has been interpreted by a process of further insertion of SiF_2 into the initially formed silirane intermediate [4,8]. Although the insertion of SiF_2 into difluorosilirane has not been proved experimentally, such reactions are believed to occur in the case of dimethylsilylene [9].

In this paper we report our study on the reactions of difluorosilylene with cyclopentadiene and cycloheptatriene, the results show direct evidence for the coexistence of the $\cdot SiF_2SiF_2 \cdot$ diradical mechanism with the silirane mechanism in the cocondensation reactions.

Results and discussion

Reaction with cyclopentadiene. The gas phase reaction of difluorosilylene with freshly prepared cyclopentadiene was carried out by the same experimental procedures as previously described [11]. Under these experimental conditions no polymerization of SiF_2 was allowed so the reactions must be reactions of monomeric SiF_2 [10].

The major product of the gas phase reaction of SiF_2 with C_5H_6 was a white polymeric material which formed a film that coated the wall of the reaction bulb. The minor volatile products, which accounted for only approximately 15% total yield, contained mainly the components **4a**, **4b**, **5a**, **5b** and **6**.



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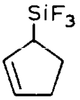

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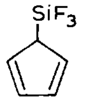

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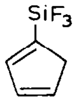

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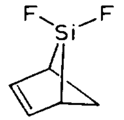


(6)

Using different separation conditions, it was possible to obtain samples of the mixtures of **4a/4b** + **5a/5b** + **6**, **4a/4b** + **5a/5b** and **4a/4b** (see Experimental). The mass spectral data suggested that there were at least three types of molecular formulae involved, $C_5H_7SiF_3$ (*m/e* 152), $C_5H_5SiF_3$ (*m/e* 150) and $C_5H_6SiF_2$ (*m/e* 132). The mass spectral data and relative yields (determined by NMR) are summarized in Table 1.

The proton noise decoupled ^{19}F NMR spectra of **4a**, **4b**, **5a** and **5b** all consisted of a sharp singlet in the typical resonance region for SiF_3 (130–145 ppm). Compounds **4a/4b** and **5a/5b** are the most likely structures for the molecular formulae $C_5H_7SiF_3$ and $C_5H_5SiF_3$, respectively. The ^{19}F NMR spectrum of **6** was complicated. When the proton noise was decoupled, the spectrum showed two doublets (with *J* 120 Hz) centered at 116.66 and 147.96 ppm, respectively. These are characteristic features of

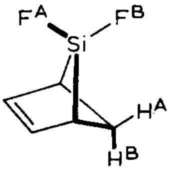
TABLE 1

MASS SPECTRAL DATA OF THE PRODUCTS FROM THE REACTION OF DIFLUOROSILYLENE WITH CYCLOPENTADIENE

Fragment	*m/e*	Relative intensity (%)						
		4a/4b + **5a/5b** + **6** [a]	**4a/4b** + **5a/5b** [b]	**4a/4b**	**7**	**7** + **8** [c]	**7** + **9** [d]	**10** + **11** [e]
SiF^+	47	40	62	35				18
$C_5H_5{}^+$	65	11	6	15	3	13	5	7
$C_5H_6{}^+ (SiF_2{}^+)$	66	98	10	18	13	100	85	12
$C_5H_7{}^+ (SiF_2H^+)$	67	100	100	100	2	23	60	45
$SiF_3{}^+$	85	23	36	46			23	2
$C_5H_6SiF^+$	113				13	10	15	6
$C_5H_6SiF_2{}^+, Si_2F_4{}^+$	132	85			9	95	45	85
$C_5H_5SiF_3{}^+$	150	8	17					
$C_5H_6SiF_3{}^+ (Si_2F_5{}^+)$	151					90	80	93
$C_5H_7SiF_3{}^+$	152	53	48	60				
$C_5H_6Si_2F_3{}^+$	179					3	5	4
$C_5H_6Si_2F_4{}^+$	198				100	97	90	
$C_5H_7Si_2F_5{}^+$	218						45	
$C_{10}H_{12}Si_2F_4{}^+$			264					100

[a] **4a/4b/5a/5b**:**6** = 3:9:1. [b] **4a/4b**:**5a/5b** = 11/4. [c] **7**:**8** = 10:3. [d] **7**:**9** = 4:1. [e] **10**:**11** = 8:1.

a bridge-head SiF_2 group in bicyclic molecules [11]. One interesting spectral feature worth mentioning is the unusually large four-bond coupling constant between F^A and H^B (J(F–H) 40 Hz) due to a double W shape relationship between the two nuclei. The NMR spectral parameters are summarized in Table 2.



The cocondensation reaction of difluorosilylene with cyclopentadiene resulted in a yellowish brown polymer (yield 48%) and a number of volatile products (yield 18%). The volatile products were separated into three fractions according to the volatility: (i) a fraction volatile at −50°C collected at −78°C, (ii) a fraction volatile at −15°C collected at −35°C and (iii) a fraction volatile at room temperature which was collected at 0°C.

Fraction (i) contained the same products as those obtained in the gas phase reaction. Fraction (ii) contained three compounds **7**, **8**, and **9** in a relative abundance ratio 20/5/1.

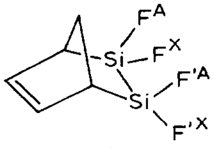
Compound **7**, a colorless crystalline material, could be purified by low temperature filtration followed by sublimation under vacuum. Both the mass spectrum and elemental analysis indicated the molecular formula $C_5H_6Si_2F_4$ (Found: C, 30.40, H, 3.14; calcd.: C, 30.33, H, 3.03%.) The proton noise decoupled ^{19}F NMR spectrum showed two sets of doublet of doublets centered at 139.49 and 147.38 ppm,

TABLE 2

NMR PARAMETERS OF PRODUCTS FROM THE REACTION OF DIFLUOROSILYLENE WITH CYCLOPENTADIENE

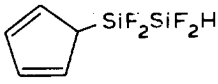
Compound	Chemical shift (δ, ppm)				Coupling constant (Hz)
	^{1}H	^{19}F	^{13}C	^{29}Si	
4a/4b	sp^2 6.2(br)	140.70(s)			
	sp^3 2.2 ~ 2.8(br)	141.16(s)			
5a/5b	sp^2 6.2 ~ 6.4(br)	138.06(s)			
	sp^3 2.5(br)	139.86(s)			
6	sp^2 5.4(br)	116.66			
		(AX)			^2J(F–F) 120
	sp^3 2.0(br)	147.96			^4J(F–H) 40 (W shape)
	1.5(br)				
7	sp^2 6.15(br)	139.49(d,d)	sp^2 131.12(s)	29.11	^2J(F–F) 30.0
				(d,d,d,d)	
	sp^3 CH 2.1(br)	147.33(d,d)	sp^3 31.85(c)		^3J(F–F) 15.0
	sp^3 CH$_2$ 2.6(br)		31.88		^1J(Si–F) 352.4, 371.5
					^2J(Si–F) 49.10, 34.25
8	sp^2 6.3(c)	SiF$_2$ 120.07(c)	sp^2 127.09(s)		^2J(H–F) 60.0
	sp^3 2.7(m)	HSiF$_2$ 137.54(c)	131.37(s)		^3J(H–F) 10.0
	SiH 4.6(t,t)		sp^3 28.0(c)		
9	sp^2 6.15(br)	SiF$_3$ 141.6(d,d)	sp^2 128.37(s)		^2J(H–F) 68.0
	sp^3 2.6(m)	SiF$_2$ 144.0	128.49(s)		^2J(F–F) 8.0
	2.8 ~ 3.0(m)	144.6 (AB,d)	sp^3 22.40(c)		
	SiH 4.73(t)		14.12(s)		
10/11	sp^2 5.6 ~ 6.0(br)	**10** 142.96			
	sp^3 1.4 ~ 1.9(br)	145.42 (AA′BB′)			
	2.1 ~ 2.8(br)				
	2.9 ~ 3.4(br)	**11** 136.49(t)			
		130.53(t)			

respectively. This is a typical AA′XX′ pattern of the SiF$_2$SiF$_2$ unit in the bicyclic structure [1,11]. Further evidence came from the ^{29}Si NMR spectrum which showed a doublet (^1J(Si–F$^{A(X)}$) 371.5 Hz) of doublets (^1J(Si–F$^{X(A)}$) 352.4 Hz) of doublets (^2J(Si–F$'^{X(A)}$) 49.10 Hz) of doublet (^2J(Si–F$'^{(AX)}$) 34.25 Hz), with F^A and F^X arbitrarily assigned to the geminal fluorines.



(7)

Compound **8** was purified by prolonged pumping off this fraction through a trap at −30°C and collected at −196°C. It was found to have the same molecular formula, $C_5H_6Si_2F_4$, as **7**. Both its ^{1}H and ^{19}F spectra showed the existence of the moiety SiF$_2$SiF$_2$H. The typically large ^1J(F–H) (60 Hz) makes the assignment easier. It was further found from the peak intensity that four unsaturated protons were involved in compound **8**, the only structure that fits these spectral features is shown below:

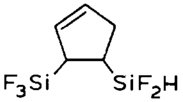


(8)

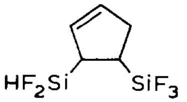
The ^{13}C NMR spectrum showed in addition to the two types of sp^2 carbons a saturated carbon at 28.0 ppm which showed multiplicity as a result of being coupled with the neighboring fluorines. This is a further piece of evidence for the structure assignment of compound **8**.

Compound **9** could not be separated completely from compound **7**. However, the highest mass in the mass spectrum (*m/e* 218) suggested that **9** had the molecular formula $C_5H_7Si_2F_5$.

Both the ^1H and ^{19}F NMR spectra of compound **9** showed typical geminal F–H coupling (68 Hz) which suggested the existence of the SiF_2H moiety. The proton decoupled ^{19}F NMR spectrum showed two resonances centered at 141.6 and 144.3 ppm with an intensity ratio 3/2. The former was a broadened doublet of doublets and the latter was an AB pattern with each peak further split into a broadened quartet. Two structures fit these spectral features entirely, but it is not possible to differentiate between these two at this moment.



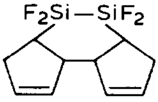
(9a)



(9b)

It is worth noting that in both cases the carbon to which the SiF_2H group is attached is an asymmetric center. This will make the two fluorines in the SiF_2H group intrinsically nonequivalent, as is evident by the AB spectrum described above.

The yield of fraction (iii) was very low. The mass spectrum showed the highest mass peak *m/e* 264, corresponding to the molecular formula $C_{10}H_{12}Si_2F_4$. The proton decoupled ^{19}F NMR spectrum showed an AA'BB'' pattern at 142.96 and 145.42 ppm, and two triplets at 136.49 and 137.53 ppm. The intensity ratio of the AA'BB' spectrum to the two triplets was roughly 8/1. Based on previous spectral assignments of similar compounds [1], the AA'BB' pattern is characteristic of an SiF_2SiF_2 unit involved in the rigid ring system **10**, while two sets of triplets are characteristic of a free rotating chain structure **11**.



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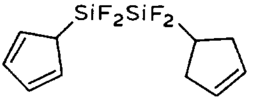


(11)

All spectral data are summarized in Table 2.

Reaction with cycloheptatriene

The gas phase reaction of difluorosilylene with cycloheptatriene yielded polymeric materials and volatile products in an approximately relative ratio of 3/2. The

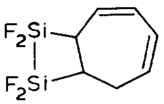
TABLE 3

MASS SPECTRAL DATA OF THE PRODUCTS FROM THE REACTION WITH CYCLOHEPTATRIENE

Fragment	*m/e*	Relative intensity (%)		
		12	**13**	**12+13+14+15** [a]
SiF_2^+	66	7		34
$C_7H_7^+$	91	90	55	3
$C_7H_8^+$	92	93	79	100
$C_7H_9^+$	93	14	7	31
$C_7H_8SiF^+$	139	7	3	
$Si_2F_5^+$	151			35
$C_7H_8SiF_2^+$	158	36	34	83
$C_7H_8SiF_3^+$	177	15	4	6
$C_7H_8Si_2F_4^+$	224	100	100	96

[a] **12**:**13**:**14**:**15** = 15:5:3:1.

volatile fraction contained mainly compound **12**, in 15% yield on the basis of the quantity of cycloheptatriene used.

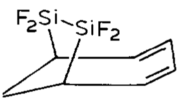


(12)

The characterization of **12** was based on the following spectral features: (i) the mass spectrum (Table 3) showed a molecular formula $C_7H_8Si_2F_4$ ($m/e = 224$); (ii) the proton decoupled ^{19}F NMR spectrum showed four doublets of doublets of doublets with equal intensity, showing that the four fluorines are nonequivalent and that the molecule did not have a plane of symmetry; (iii) the ^{13}C NMR spectrum showed four sp^2 carbons at 121.81, 131.42, 132.19 and 132.83 ppm, two sp^3 carbons with fluorine coupling at 28.00 and 33.63 ppm, and one saturated CH_2 carbon at 25.55 ppm; and (iv) the n-hexane solution of **12** showed a broad absorption with λ_{max} at 250 nm which is typical of a cyclic conjugated diene system. The only structure that fits all these spectral data is **12**.

The mass spectral results of the reactions with cycloheptatriene are listed in Table 3 and NMR spectral results in Table 4.

The cocondensation reaction of difluorosilylene with cycloheptatriene yielded a reddish brown polymer. The volatile fraction (about 10% yield) contained mainly three compounds, **13**, **12** and **14**, with relative yields in a 20/2/1 ratio. A trace amount of compound **15** was also present in this fraction.



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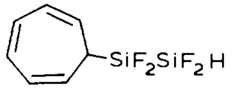

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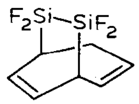


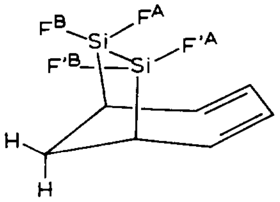
(15)

TABLE 4

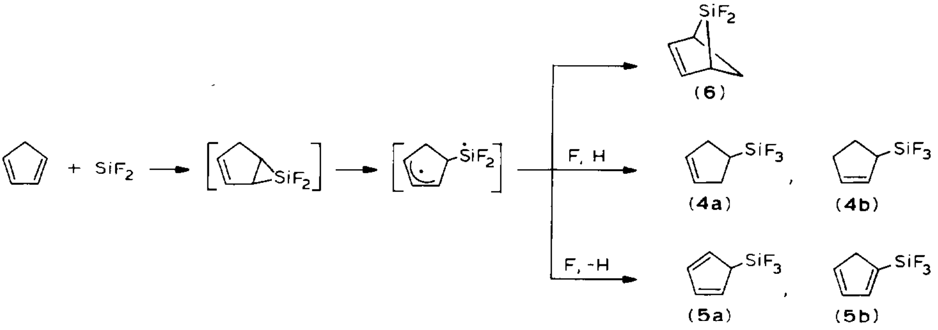
NMR PARAMETERS OF PRODUCTS FROM THE REACTION OF DIFLUOROSILYLENE WITH CYCLOHEPTATRIENE

Compound	Chemical shift (δ (ppm))			Coupling constant (Hz)
	^1H	^{19}F	^{13}C	
12	sp^2 5.6 ~ 6.1(br)	54.98 (d,d,d)	sp^2 121.81(s)	^2J(F–F) 32
	sp^3 3.6(br)	55.17 (d,d,d)	131.42(s)	^3J(F–F) 14 (*trans*)
	2.0 ~ 2.5(br)	55.90 (d,d,d)	132.19(s)	^3J(F–F) 7 (*cis*)
		56.17 (d,d,d)	132.83(s)	
			sp^3 CH 28.00(c)	
			33.63(c)	
			CH_2 25.55(s)	
13	sp^2 5.8 ~ 6.1(br)	54.24 (d,d,d)	sp^2 124.63(s)	^2J(F–F) 21
	sp^3 2.7(br)	55.83 (d,d,d)	126.80(s)	^3J(F–F) 14
	1.9 ~ 2.3(br)		sp^3 CH 31.00(c)	^4J(F–H) 7
			CH_2 24.49(s)	
14	sp^2 5.8 ~ 6.1(br)	56.22(t)		^2J(F–H) 53
	sp^3 2.7(br)	55.32(d,t)		^3J(F–F) 6
	SiH 4.7(t,t)			
15		54.93(d,d,d)		^2J(F–F) 35
		55.51(d,d,d)		^3J(F–F) 18
		56.26(d,d,d)		
		56.72(d,d,d)		
16		55.13(AB,d)		^2J(F–H) 68
		55.27(br.s)		

Compound **13** was obtained in a pure crystalline form by fractional crystallization followed by vacuum sublimation. The mass spectrum suggested a molecular formula $C_7H_8Si_2F_4$. The ^{13}C NMR spectrum showed two sp^2 carbons (δ 124.63 and 126.80 ppm), one saturated CH with fluorine couplings (δ 31.00 ppm) and one saturated CH_2 at δ 24.49 ppm. It is obvious from these data that the molecule has a plane of symmetry. The proton decoupled ^{19}F NMR spectrum showed an AA′BB′ pattern at 54.24 and 55.83 ppm respectively. The resonance at 55.83 ppm obviously showed a long range F–H coupling of 7 Hz which was best explained by the W shape of the F–Si–CH–C–H arrangement, therefore the resonance at 55.83 ppm must be assigned to F^A and F'^A.



Compound **14** showed in its mass spectrum the highest mass peak at $m/e = 224$, corresponding to the molecular formula $C_7H_8Si_2F_4$. Both ^1H and ^{19}F NMR spectra showed the large geminal H–F coupling of 53 Hz, which was characteristic of the SiF_2H moiety. The proton decoupled ^{19}F NMR spectrum showed a strongly coupled A_2B_2 pattern which suggested the existence of SiF_2SiF_2H. The most likely structure is **14**.

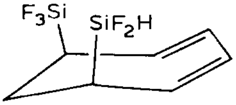


SCHEME 1

Compound **15** was obtained only in a trace amount. However, the well separated ^{19}F NMR spectrum definitely showed four broadened doublets of doublets at 54.93, 55.51, 56.26 and 56.72 ppm. This is the typical pattern of the bridge-head SiF_2SiF_2 unit; further, since the four fluorines are chemically nonequivalent, the molecule does not have a plane of symmetry. It seems quite certain that the only structure of this kind other than compound **12** is compound **15**.

It is interesting to note that when an n-hexane solution of **13** was UV irradiated at −30°C for 12 h, it was converted to **12** almost quantitatively.

Compound **13** was not very stable in solution. It converts to **16** at room temperature even when kept in a vacuum-sealed tube.



(**16**)

Compound **16** was fully characterized by mass spectrometry and ^{19}F NMR spectra. The mass spectrum suggested a molecular formula $C_7H_9Si_2F_5$ whereas the ^{19}F NMR spectrum showed a singlet and a doublet at 55.13 and 55.27 ppm respectively for SiF_3 and SiF_2 (intensity ratio 3/2), with the latter showing a large geminal F–H coupling of 68 Hz.

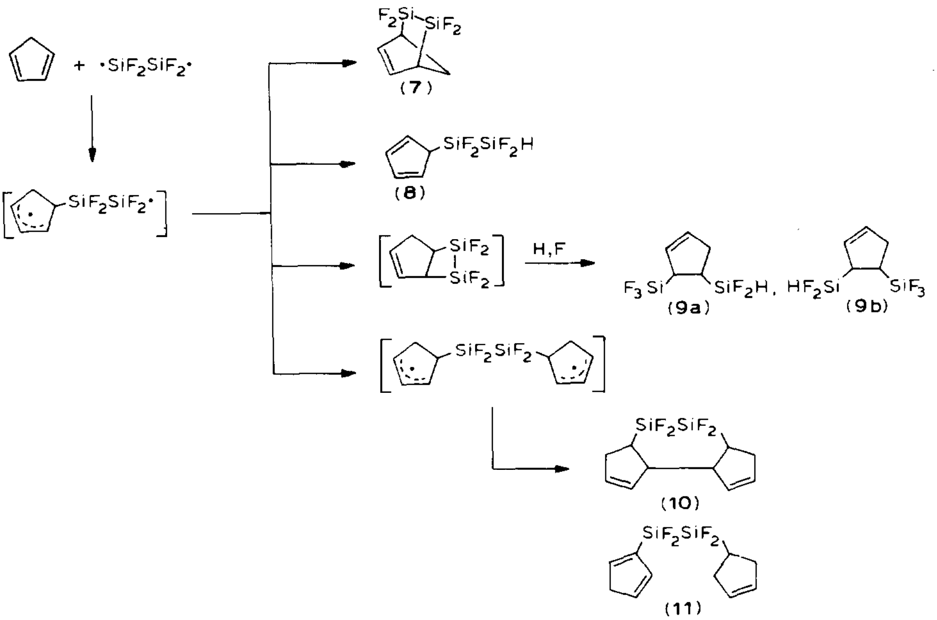
In the reaction with cyclopentadiene it is believed that products **4**–**6** were formed via the generally accepted silirane intermediate [4] as is shown in Scheme 1.

Despite differences in the reaction conditions, it is interesting to note that the silirane intermediates intially formed in thermal reactions of dimethylsilylene and dichlorosilylene with cycloheptadiene rearrange to give silacyclohexadienes [12,13]. No product analogous to structure **6** was reported.

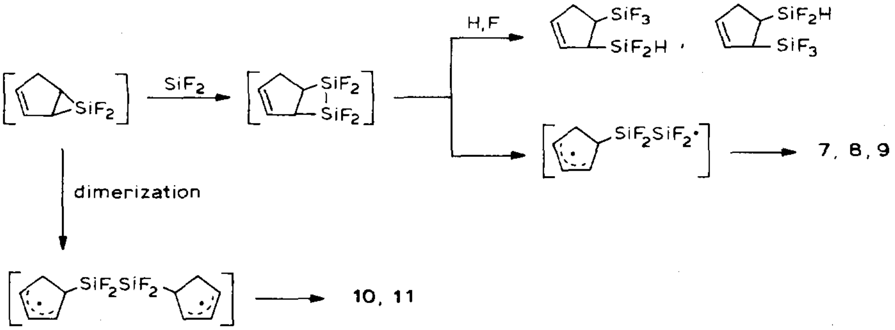
The formation of products **7**–**11** is best interpreted by the mechanism involving the $\cdot SiF_2SiF_2\cdot$ diradical as is shown in Scheme 2.

However, all these products may also be explained by the mechanism involving a silirane intermediate (Scheme 3).

In the gas phase reaction with cycloheptatriene, however, compound **12** was obtained. This is the first time that a compound involving the $-SiF_2SiF_2-$ unit is obtained as the major product in a gas phase reaction of difluorosilylene [14]. Since

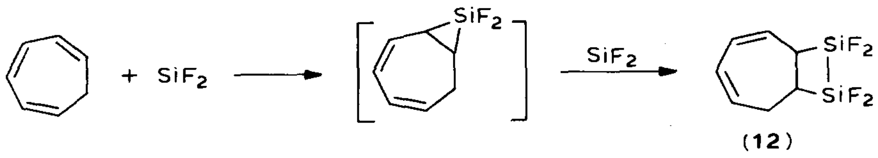


SCHEME 2

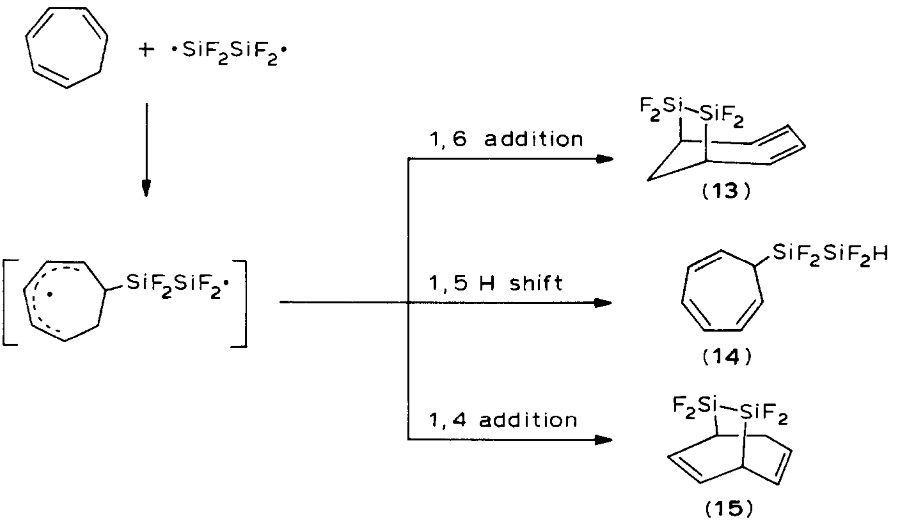


SCHEME 3

formation of oligomeric $(SiF_2)_n$ was not likely under the experimental conditions used in the gas phase reactions, the logical explanation for the formation of **12** is as shown in Scheme 4.



SCHEME 4

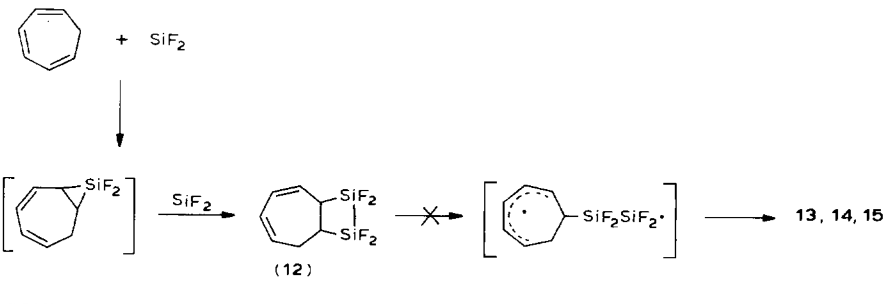


SCHEME 5

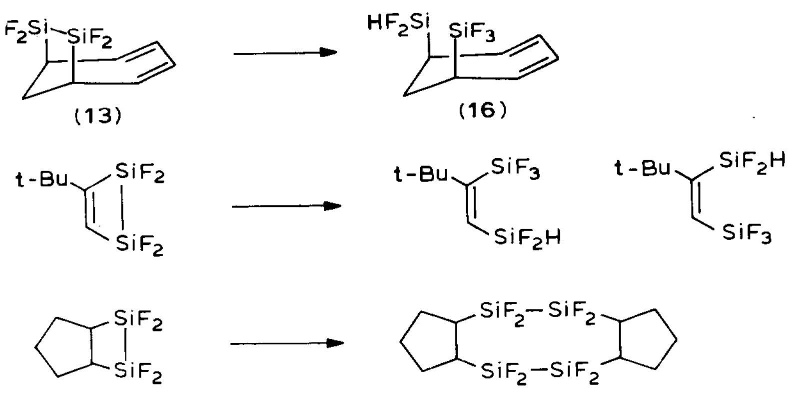
The formation of compounds **13–15** obtained in the cocondensation reaction is best explained by the mechanism involving the SiF_2SiF_2 diradical (Scheme 5).

The interpretation of the formation of **13–15** by the silirane mechanism is difficult (Scheme 6). Product **12** is a stable compound which did not lead to the formation of **13–15** under the experimental condition used. If the cocondensation reaction proceeded in a similar way to the reaction mechanism in the gas phase reaction (Scheme 4), one would expect that the major product in the cocondensation reaction was also **12**. However, the major product in the cocondensation reaction was found to be **13** (85% relative yield), which could not be formed by sequential addition of SiF_2 unless very skeptical assumptions were made. One therefore tends to believe that at least in the case of the cycloheptatriene reaction, the SiF_2SiF_2 diradical mechanism is mainly responsible for the formation of **13–15**. It seems to us that this is the first solid evidence which makes it possible to differentiate between the two mechanisms in the addition reactions of difluorosilylene.

Returning to the rationalization of the cyclopentadiene cocondensation reaction by the silirane mechanism (shown in Scheme 3), the formation of the diradical species leading to **7**, **8**, and **9** is doubtful given the present argument. It was



SCHEME 6



SCHEME 7

proposed in Scheme 3 that the diradical species was generated by C–Si bond cleavage of the disilacyclobutane intermediate. The experimental facts depicted in Scheme 7 strongly indicate that such strained disilacycles seem to favor the Si–Si cleavage much more than the C–Si cleavage [15].

Experimental

All reactions were carried out in a greaseless vacuum system similar to that used for previous studies of difluorosilylene chemistry described elsewhere [1,2]. All reagents were commercial products and used without further purification. Cyclopentadiene was freshly distilled from the mixture of its dimer before use.

The gas phase reactions were carried out in a previously evacuated 6 l bulb. Each run lasted for 25 min, approximately 10 times the half life of SiF_2 in the gas phase [14]. Reactions carried out under such conditions are believed to involve only monomeric SiF_2.

Reaction with cyclopentadiene

When the products from the gas phase reaction with cyclopentadiene were subjected to prolonged pumping at −78°C, compound **6** was removed from the mixture as pure material. A sample containing only **4a** and **4b** was obtained by washing the polymers which coated the wall of the reaction bulb with chloroform.

The products of the cocondensation reaction with cyclopentadiene were separated into three fractions as is described in the text. The relative yields of the fractions were estimated by NMR integration to be 10/85/5.

Reaction with cycloheptatriene

The gas phase reaction with cycloheptatriene yielded mainly one product, **12**, which was further purified by prolonged pumping at −10°C. The yield was approximately 15%.

The products of the cocondensation reaction with cycloheptatriene were further purified by pumping at −10°C. The crystals on the wall of the U-tube were subjected to vacuum sublimation which yielded compound **13**. A reasonably pure sample of **14** was obtained by washing the crystals at −45°C with n-pentane (both

12 and **13** remained crystals at −45°C in n-pentane solution). All operations were carried out in a vacuum system fitted with a sintered glass filter.

Spectra

The mass spectra were obtained using a JMS 100 mass spectrometer. The ^{1}H, ^{19}F, ^{13}C, ^{29}Si NMR spectra were recorded on a JNM FX-100 spectrometer operating at 99.60, 93.70, 25.05 and 19.75 MHz, respectively. In all cases $CDCl_3$ was used as the solvent. Chemical shifts of ^{1}H, ^{13}C and ^{29}Si were measured with TMS as internal reference, those of ^{19}F were measured in ppm upfield from the internal reference, CCl_3F.

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