Journal of Organometallic Chemistry, 226 (1982) 21—34
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

REACTIONS OF DIFLUOROSILYLENE WITH CYCLOPENTENE AND CYCLOHEXA-1,3-DIENE

YI-MING PAI, CHENG-KWANG CHEN and CHAO-SHIUAN LIU *
Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan (Rep. of China)

(Received June 18th, 1981; in revised form October 5th, 1981)

Summary

The cocondensation reactions of difluorosilylene with cyclopentene and cyclohexa-1,3-diene have been studied. Several new organosilacyclic compounds were synthesized and their structures characterized. In all but one case the products contain SiF_2SiF_2 linkage. One of the products from the reaction of cyclohexa-1,3-diene is shown to undergo thermal decomposition which leads to the formation of perfluoropolysilacycles, $(SiF_2)_n$ ($n = 3, 4, 5$). The polymers formed in the reaction of cyclopentene are shown to have $(C_5H_8SiF_2)$ repeating units. The reaction mechanism is discussed.

Introduction

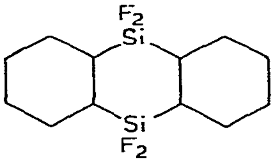
The cocondensation reactions between difluorosilylene and methyl-substituted ethylenes have been reported recently [1,2]. The reaction mechanism has been explained by Thompson with the initial formation of the silirane intermediate, followed by either further SiF_2 addition (to form disilacyclobutanes) or ring opening (to form all other products resulting from the diradical species) [1]. However, from comparison of the results of cocondensation and gas-phase reactions of halogen-substituted ethylenes [3], it has been quite conclusively demonstrated that in addition to the involvement of silirane intermediates, diradicals $^{\cdot}(SiF_2)_n{}^{\cdot}$ ($n = 2, 3, ...$) must also play an important role in the cocondensation reactions.

Only one diene reaction has been studied, that of 1,3-butadiene [4,5]. The major products in the cocondensation reaction and the gas-phase reaction are 1,2-disilacyclohex-4-ene and silacyclopent-3-ene, respectively. Again, the former can be explained by the 1,4 addition of a $^{\cdot}SiF_2SiF_2{}^{\cdot}$ diradical whereas the latter is best viewed as a result of the rearrangement of the initially formed silirane, which is attached with a vinyl group in this particular case.

It is therefore desirable to extend this study to other olefins in order to see

0022-328X/82/0000—0000/$02.75

whether this reaction mechanism is generally applicable, for example, to cyclic olefins. The preliminary results [6] of the cocondensation reaction between difluorosilylene and cyclohexene suggested that the product has a structure as shown below:



This reaction pattern is analogous to that of dimethylsilylene [7] but has never been observed in the cocondensation reactions with SiF_2. Obviously more studies on cycloalkenes are needed. This paper reports our results on the reactions of difluorosilylene with cyclopentene and cyclohexa-1,3-diene.

Experimental

Reactions

All reactions were carried out in a greaseless vacuum system similar to that used for previous studies of difluorosilylene chemistry described elsewhere [7]. All reagents were commercial products used without further purification.

The reaction of cyclopentene gave a reddish brown condensate at −196°C which turned to light yellow polymers on warming to room temperature. The volatile products were separated from unreacted SiF_4 and C_5H_8 by passing through a trap at −78°C. The products were then subjected to further fractionation. Two fractions were obtained as follows: (i) the fraction volatile at 0°C collected at −22°C contained mainly compound I, and a small amount of II, (ii) the fraction volatile at room temperature and collected at 0°C contained mainly compound IV and a small amount of III, (iii) the fraction collected at room temperature contained compound V. The total yield including polymers was about 60%, of which volatile products accounted for 30%. The relative yields of the fractions were estimated to be 20/30/50.

The reaction of cyclohexa-1,3-diene gave a dark brown condensate at −196°C which turned to yellow polymers on warming to room temperature. The volatile products were separated from the unreacted SiF_4 and C_6H_8 by passing through a trap at −78°C. Small amount of C_6H_8 was not removed by this procedure. However, C_6H_8 could be removed by pumping through a trap at −45°C at the expense of some more volatile products. The following conditions were employed for product separation: (i) the fraction volatile at −35°C and −55°C contained compound VI, (ii) the major component in the fraction which was volatile at −20°C and collected at −35°C was compound VII, and (iii) the fraction volatile at room temperature and collected at 0°C contained compound VIII. The total yield including the polymers was about 65%, of which the volatile products account for 35%. The relative yields of three fractions were estimated to be 15/45/40.

Spectra

The mass spectra were obtained using a JMS 100 mass spectrometer. The ^1H,

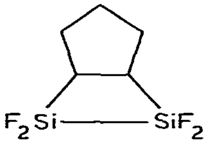
^{19}F, ^{13}C NMR spectra were recorded on a JNM FX-100 spectrometer operating at 99.60, 93.70 and 25.05 MHz, respectively. The ^{29}Si spectra were obtained from a Varian 80A spectrometer operating at 15.80 MHz. In all cases, $CDCl_3$ was used as the solvent. Chemical shifts of ^1H, ^{13}C and ^{29}Si were measured with a tetramethylsilane (TMS) internal reference, those of ^{19}F were measured in ppm upfield from the internal reference CCl_3F.

Results and discussion

Reactions with cyclopentene

The fraction, volatile at 0°C and collected at −22°C, accounts for about 10% of the total products. The mass spectrum of this fraction shows the highest mass peak at *m/e* 200 (Table 1), which corresponds to a molecular formula of $C_5H_8Si_2F_4$.

The ^1H, ^{19}F, ^{13}C and ^{29}Si NMR spectral data are summarized in Table 2. All ^1H resonances correspond to saturated CH. The ^{19}F NMR spectrum shows an AA'BB' pattern on ^1H-decoupling. The ^{13}C NMR shows two singlets at δ 20.6 and 25.0 respectively, and a resonance at δ 26.1 which resembles a quintet due to F couplings. All these data conslusively indicate that the compound has structure I.



(I)

The ^{29}Si NMR spectrum of I shows a triplet of triplets at 126.66 ppm, which is unambiguous evidence of the direct linkage of the two SiF_2 units.

(*Continued on p. 26*)

TABLE 1

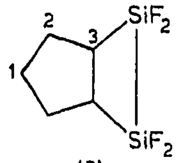
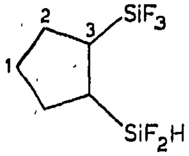
MASS SPECTRAL DATA [a] OF COMPOUNDS I, III, IV AND V

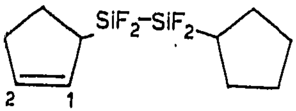
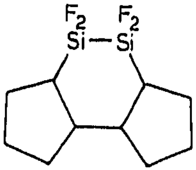
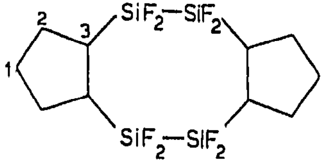
Fragment	*m/e*	Abundance			
		I	III	IV	V
SiF^+	47	25	10	5	1
$C_5H_7^+$, (SiF_2H^+)	67	50	80	68	70
$C_5H_8^+$	68	100	100	100	100
$C_5H_8SiF_2^+$	115		30	9	
$C_5H_8SiF_2^+$	134	62	60	70	70
$C_5H_8SiF_3^+$	153	40	48	50	49
$C_5H_8Si_2F_4^+$	200	6		12	90
$C_5H_9Si_2F_4^+$	201		14	5	
$C_5H_8Si_2F_5^+$	219				23
$C_5H_8Si_3F_6^+$	266				32
$C_{10}H_{16}Si_2F_4^+$	268		30	24	
$C_5H_8Si_4F_8^+$	332				11
$C_{10}H_{16}Si_4F_8^+$	400				10

[a] 12 eV.

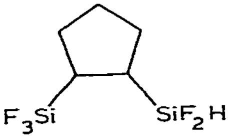
TABLE 2

NMR SPECTRAL DATA OF COMPOUNDS I, II, III, IV AND V

	δ(1H) (ppm)		δ(^{19}F) (ppm)			δ(^{13}C) (ppm)			δ(^{29}Si) (ppm)	Coupling constant (Hz)		
 (I)	H1	2.0(br)	F	128.6	($A_2A'_2$)	C1	25.0(s)		−126.66(t,t)	J(C—F)		10.5
	H2	2.3(br)				C2	20.6(s)			^1J(Si—F)		417.5
	H3	1.8(br)				C3	26.1	($AA'X_2X'_2$)		^3J(Si—F)		35.5
 (II)	H1	2.0(br)	SiF_3	138.9(t,m)						^2J(H—F)		68.0
	H2	2.3(br)	SiF_2	143.0	(AB,d,q)					^5J(H—F)		4.0
	H3	1.8(br)		143.8						^2J(F—F)	(AB)	6.9
	SiH	4.9(t,q)								^5J(F—F)		4.2

 (III)	H(sat)	1.5—2.5(br)	SiF$_2$	137.5	(A$_2$X$_2$)	C(sat)	26—30(s)			
	H1	5.8(d,m)		138.2		C1	146.3(s)			
	H2	6.8(br)				C2	119.1(s)			
 (IV)	all H	1.5—2.4(br)	F	136.6	(AA'XX')	all C	16.6—28.5			
				140.1						
 (V)	H1	2.0(br)	F	141.6	(AA'XX')	C1	26.4(s)	−103.50(t,t)	J(C—F)	10.6
	H2	2.3(br)		146.1		C2	27.5(s)		${}^1J$(Si—F)	356.5
	H3	1.8(br)				C3	29.2 (AA'X$_2$X'$_2$)		${}^3J$(Si—F)	48.9

Careful examination of the spectra of this fraction reveals that another minor component (about 5% of the fraction) with a molecular formula $C_5H_9Si_2F_5$ is mixed in the fraction. The characteristic feature in the ^{1}H NMR spectrum is the triplet of quartets at δ 4.9 ppm, with the coupling constant of 68 Hz for the triplet and 4.2 Hz for the quartets. This is a strong evidence for the existence of the SiF_2H group being adjacent to an SiF_3 group in the molecule.



(II)

The structure of II is confirmed by its ^{19}F NMR spectrum (Fig. 1). The SiF_3 resonance is shown as a triplet (^5J(F—F) 4.2 Hz) in the proton-decoupled spectrum. The SiF_2H group shows basically an AB spectrum being split into a doublet (68 Hz) by the geminal H and quartets (4.2 Hz) by the SiF_3 fluorines five bonds away.

The fraction that is volatile at room temperature and collected at 0°C contains two major products. When the fraction was subjected to further purification by prolonged pumping through a trap at 0°C, a small quantity of pure III was collected at —196°C. This compound shows in the mass spectrum a

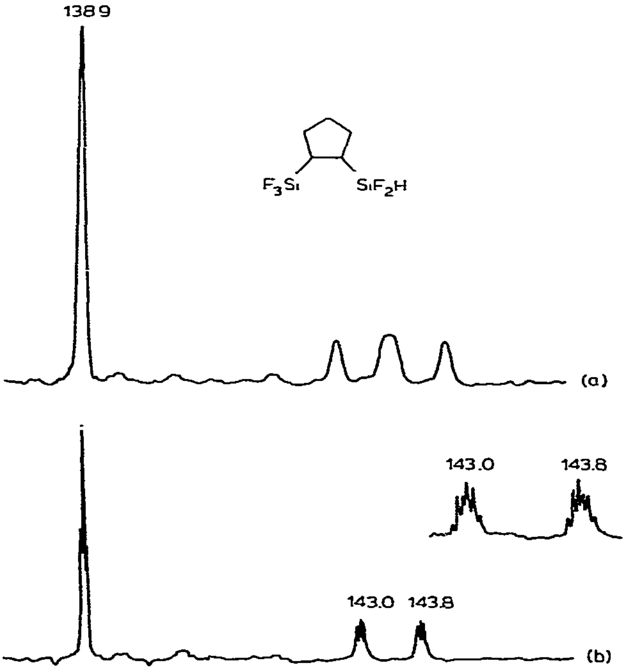
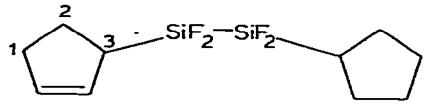


Fig. 1. (a) ^{19}F NMR spectrum of compound II. (b) ^{1}H-decoupled ^{19}F NMR spectrum compound II.

molecular formula of $C_{10}H_{16}Si_2F_4$ (Table 1).

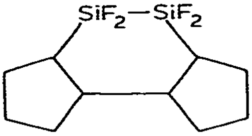


(III)

The NMR spectral data of III are summarized in Table 2. The most informative result is the ^{13}C NMR spectrum. The peaks at δ 146.3 and 119.1 ppm undoubtedly arise from two sp^2 hybridized carbons in the molecule. The other possible structure with the double bond at position 1 rather than 2 of the cyclopentenyl ring is not favored, since the vinyldisilyl moiety in such a structure would show in the ^{13}C NMR spectrum the characteristic ^{13}C—F couplings for the double bond carbons.

The material left in the trap kept at 0°C was a mixture of III and IV. Compound IV has not been obtained pure.

The mass spectral data suggest that it is an isomer of III. The NMR spectral parameters are listed in Table 2. The most informative data is the AA′XX′ pattern at 136.6 and 140.1 ppm in the ^{19}F NMR spectrum, which is characteristic for the SiF_2SiF_2 linkage in a ring system.

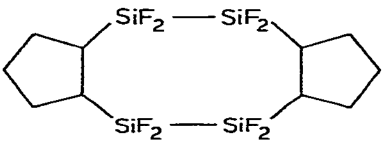


(IV)

The ^{13}C NMR spectrum of IV shows complex peaks from δ 16.64 to 28.49, all for saturated carbons. The complexity suggests that there are probable more than one isomer of IV. However, no conclusion can be made at this moment.

There remained an oily product which is slightly volatile at room temperature. The mass spectrum of this compound suggests a molecular formula of $C_{10}H_{16}Si_4F_8$ (Table 1). The ^1H NMR spectrum shows that all protons are on saturated carbons.

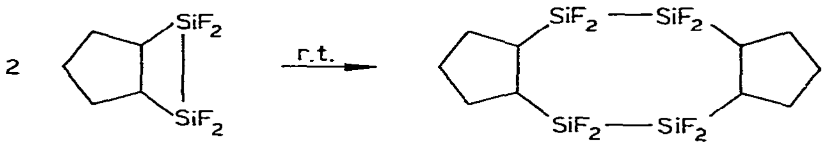
The ^{19}F NMR spectrum shows at 141.6 and 147.1 ppm an AA′XX′ pattern. The ^{29}Si NMR spectrum shows a triplet of triplets with Si—F coupling constants 356.5 and 48.9 Hz respectively. These spectral data strongly suggest that V has a ring structure as shown:



(V)

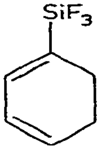
Compound I is not very stable thermally. At room temperature, I slowly converts to V and other unidentified compounds in small quantities in one week. This transformation can be unambiguously followed by both ^{13}C and

^{29}Si NMR spectra.



Reaction with cyclohexa-1,3-diene

The volatile compounds that passed through a trap of —22°C and were collected at —78°C contained at least two major products. One of the products could be obtained in pure form by further fractionation of this fraction through a trap at —35°C and collecting at —55°C. The mass spectrum of this compound shows a molecular formula of $C_6H_7SiF_3$ (Table 3). The ^{1}H NMR spectrum shows vinyl protons at δ 5.8—6.2 ppm and saturated CH resonances at δ 2.0 ppm, with approximate intensity ratio 3/4. The ^{19}F NMR spectrum of this compound shows a triplet at 142.38 ppm which reduces to a singlet on ^{1}H decoupling. The structure that fits all these spectral data is shown as VI.



(VI)

The other major product of the fraction collected at —78°C could be obtained in fair purity by prolonged pumping of the material left in the trap at —35°C

TABLE 3

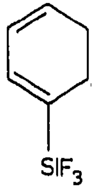
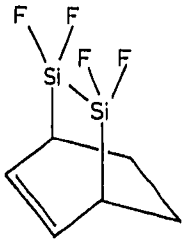
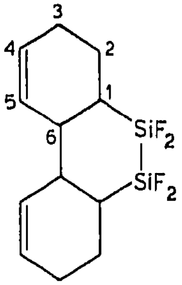
MASS SPECTRAL DATA [a] OF COMPOUNDS VI, VII, VIII AND $(SiF_2)_n$.

Fragment	m/e	Abundance				
		VI	VII	VIII	$(SiF_2)_3$	$(SiF_2)_4$
SiF_2^+	66				73	83
$C_6H_7^+$	79	100	100	46		
$C_6H_8^+$	80	80	38	100		
$Si_2F_4^+$	132				15	26
$si_2F_4H^+$	133				45	
$C_6H_8SiF_2^+$	146	5	8	15		
$C_6H_9SiF_2^+$	147			28		
$Si_2F_5^+$	151				8	2
$C_6H_7SiF_3^+$	164	68	18	4		
$C_6H_8SiF_3^+$	165		20	7		
$Si_3F_6^+$	198				100	100
$C_6H_8Si_2F_4^+$	212		42	21		
$C_6H_9Si_2F_4^+$	213			40		
$C_{12}H_{16}SiF_2^+$	226			9		
$Si_4F_8^+$	264					41
$C_{12}H_{16}Si_2F_4^+$	292			24		

[a] 12 eV.

TABLE 4

NMR SPECTRAL DATA OF COMPOUNDS VI, VII AND VIII

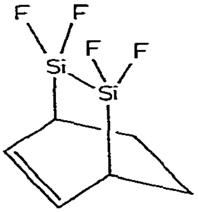
	$\delta(^{1}H)$ (ppm)		$\delta(^{19}F)$ (ppm) [a]			$\delta(^{13}C)$ (ppm) [a]		
 (VI)	CH	~2.0(br)	F	142.38 (t)				
	CH(sp^2)	5.8—6.2(c)						
 (VII)	CH	~2.0(br)	F	141.85 (d,d)				
	CH	~2.2(br)		148.04 (d,d)				
	CH(sp^2)	~6.3(c)						
 (VIII)	H2	~1.8(br)	F	139.18	} (AA'XX')	C1	27.79(m)	(29.79(m))
	H3	~2.1(br)		142.81		C2	22.51	(21.32)
	H4,5	5.85(AB)		(139.60)	} (AA'XX')	C3	23.90	(23.92)
	H1,6	~2.8(br)		(144.56)		C4,C5	129.47	(129.11)
							130.45	(130.30)
						C6	40.35	(40.42)

---

[a] Chemical shifts in parentheses belong to an isomer of VIII, see text.

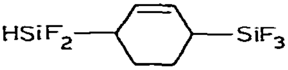
from the preceding procedure, through a trap at —20°C and collecting at —35°C. The mass spectrum of this fraction suggests a molecular formula of $C_6H_8Si_2F_4$ (Table 3).

The NMR spectral data are listed in Table 4. In the ^{1}H NMR spectrum the spectral pattern of the vinyl protons at δ 6.30 is characteristic for chemical equivalent but magnetic nonequivalent protons, which show complex virtual couplings. This may indicate a plane of symmetry in the molecule. The ^{19}F NMR spectrum shows two doublets of doublets, suggesting the two F atoms in each SiF_2 unit are chemically nonequivalent. Structure VII agrees with all these data.



(VII)

A small quantity of another compound, perhaps resulting from the decomposition of VII, was found in mixture with VII. The compound shows in both its ^{1}H and ^{19}F NMR spectra the characteristic features of a SiF_2H group (triplet at δ 4.85 ppm in ^{1}H NMR and doublets at 137.9 and 138.2 ppm in ^{19}F NMR spectra, respectively, in both cases ^2J(HF) 52 Hz). According to the reaction pattern of cyclopentene, this observation may imply the existence of

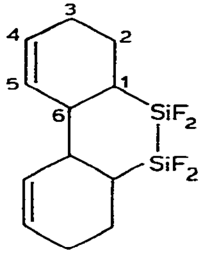


However, this structure is uncertain at present because the rest of the spectra of this compound can not be resolved from that of VII.

The fraction that was volatile at room temperature and collected at 0°C contained mainly an oily liquid of the molecular formula $C_{12}H_{16}Si_2F_4$, as was suggested by the mass spectral data (Table 3).

The ^{1}H NMR spectrum shows an AB system at δ 5.85 ppm (assigned to vinyl protons) which is further complicated by long-range couplings, and broad resonance areas at δ 2.80, 2.10 and 1.86 ppm. The latter were the resonances of the protons on saturated carbons. The ^{19}F NMR spectrum shows two sets of AA'XX' spectra at 139.18, 142.81 ppm and 137.60, 144.56 ppm, respectively, (with approximately 2/1 intensity ratio). This is strong evidence for the SiF_2SiF_2 moiety in the molecule. The ^{13}C NMR spectrum is complicated, consisting of two sets of six signals. These spectral features strongly suggest that the fraction contains two geometrical isomers of compound VIII, with relative abundance 2/1.

According to the structure of VIII, all six carbon atoms are in different chemical environments (Table 4). In each set, carbon 1 is easily assigned by the coupling with the adjacent SiF_2 groups. Carbons 2 and 3 are expected to be



(VIII)

the most shielded ones; they can be distinguished by the broadening of the peak of carbon 2. Methyne carbon 6 occurs at lower field; again, it is characterized by the obvious broadening by F couplings three bonds away. Carbon atoms 4 and 5 are sp^2 hybridized and therefore are clearly found downfield in the spectrum. The spectrum is shown in Fig. 2.

As is mentioned in the Introduction, the preliminary report [6] on the reaction between difluorosilylene and cyclohexene suggested the structure of the product as shown, whose analogy was not observed in the present reaction. The spectroscopic evidence in the present study conclusively show that the two SiF$_2$ units are linked together.

The existence of more than one geometric isomer of compound VIII is expected in view of the geometric discrimination on the linkages caused by ring closure. In fact, the reason that only two isomers are detected remains uncertain.

Compound VII is not very stable at room temperature. It decomposes overnight in a vacuum sealed sample tube into cyclohexadiene, SiF$_4$, and small quantities of at least three other products. The mass spectra of these compounds strongly suggest that they have the molecular formula (SiF$_2$)$_3$, (SiF$_2$)$_4$ and a very small amount of (SiF$_2$)$_5$ (Table 3). These three compounds were

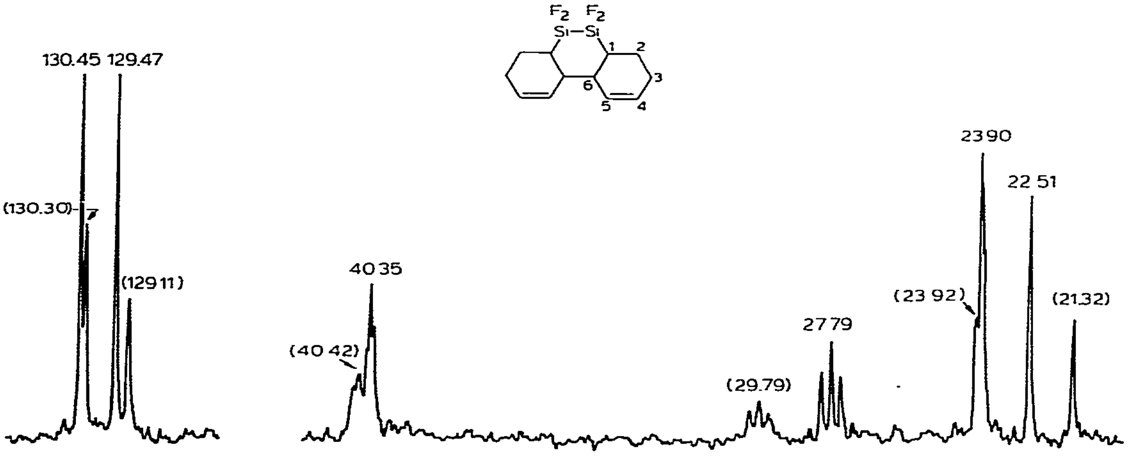


Fig. 2. ^{13}C NMR spectrum of compound VIII. Chemical shifts in parentheses belong to a geometrical isomer of $C_{12}H_{16}Si_2F_4$.

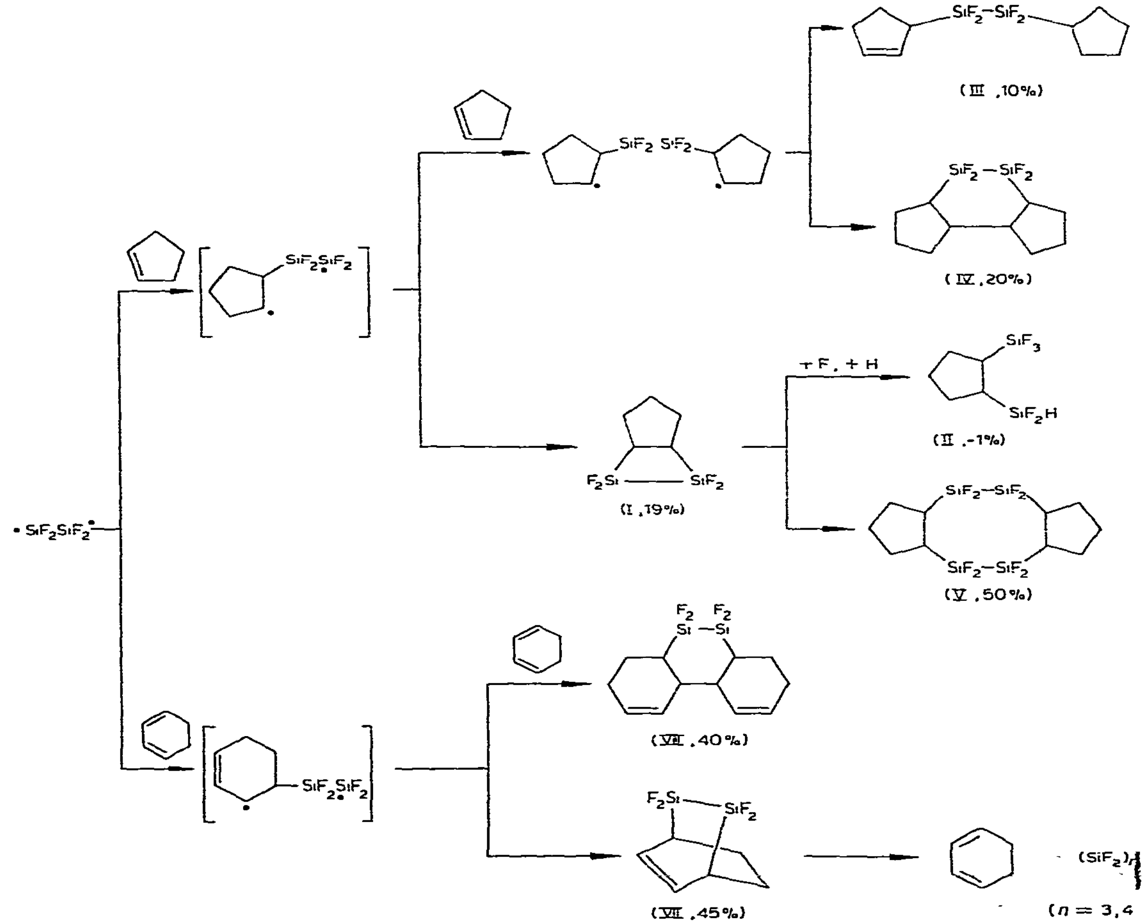
not isolated pure. Exhaustive vacuum fractionation resulted in different abundances in different samples. All three compounds show singlets in the ^{19}F NMR spectra. Based on the volatilities, the singlets at 121.05, 157.33 and 128.93 ppm are tentatively assigned to $(SiF_2)_3$, $(SiF_2)_3$ and $(SiF_2)_5$, respectively. It is the first time we observe these perfluoropolysilacyclic compounds.

The polymers

Since in both reactions the nonvolatile products account for no less than 65% of the total yields, a study of these polymers is of interest. The polymeric material formed in the reaction of cyclohexa-1,3-diene was only slightly soluble in organic solvents. Therefore no meaningful spectral data have been obtained. Fortunately, the polymers formed in the reaction of cyclopentene were much more soluble and the NMR study of the structure was possible.

The ^1H, ^{13}C NMR spectra of the soluble polymers all show very broad peaks for saturated hydrocarbons. The ^{19}F NMR spectrum shows extremely

SCHEME 1



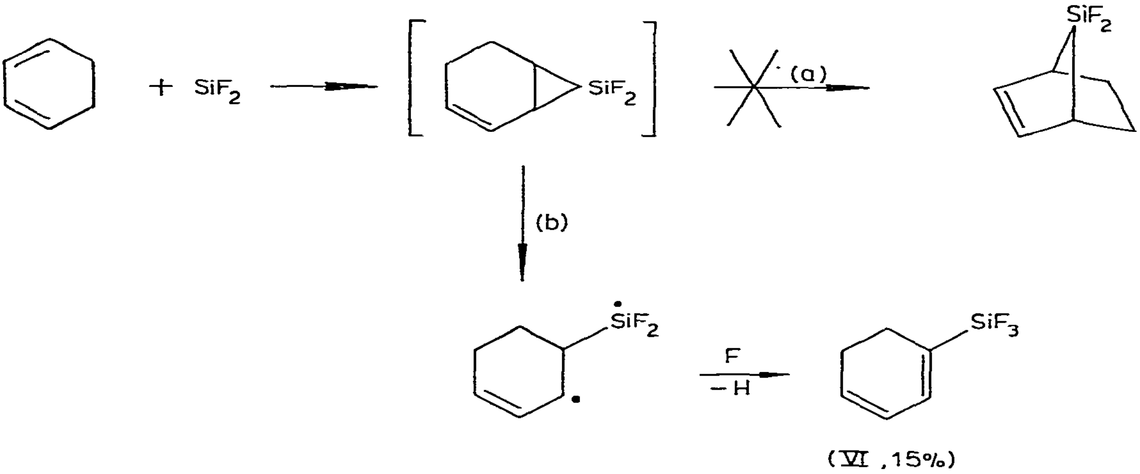
complex resonances spreading in the range of 134—152 ppm. However, the ^{29}Si spectrum shows three well-resolved triplets at —128.07, —129.18 and —130.27 ppm, with ^{1}J(Si—F) 317, 315 and 312 Hz, respectively. The observation of triplets rather than triplets of triplets is strong evidence that the polymers, at least for the soluble ones, are composed of $(C_5H_8SiF_2)_n$ units [10]. Considering the structure of such a polymer on a random basis of linkage, there are three possible arrangements for SiF_2 which show distinct chemical environments, namely, the *trans-trans*, *trans-cis*, and *cis-cis* linkages. This is in accord with three distinct triplets in the ^{29}Si NMR spectra of the soluble polymers.

The reaction mechanism

All products except compound VI can best be explained by a mechanism involving the $^{\bullet}SiF_2SiF_2^{\bullet}$ diradical intermediate (Scheme 1).

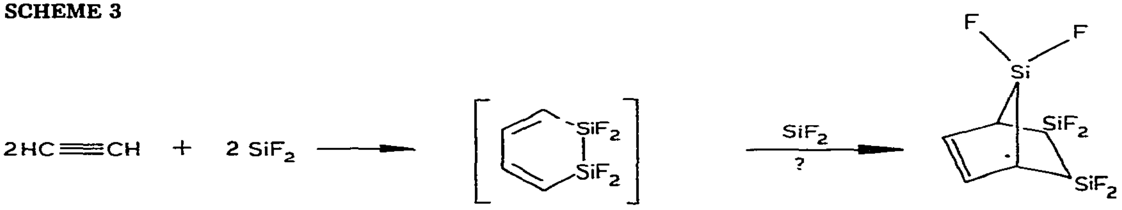
The formation of VI, and the $(C_5H_8SiF_2)_n$ structure of the polymers in the reaction of cyclopentene, strongly suggest that the silirane intermediate is also involved [8] (Scheme 2).

SCHEME 2



Although the mechanisms are not at all certain at this point, the abstraction of an F atom and elimination of an H atom are not uncommon in these reactions [2]. It is interesting to note that path (a) in the above reaction scheme was not observed. In the cocondensation reaction between difluorosilylene and acetylene, the formation of 1,1,2,2,7,7-hexafluoro-1,2,7-trisilanorborn-5-ene was assumed as a result of the further addition of monomeric SiF_2 on 1,1,2,2-tetrafluoro-1,2-disilahexa-3,5-diene [9] (Scheme 3).

SCHEME 3



The absence of the product via path (a) probably means that the above rationalization may have to be reconsidered.

Acknowledgement

The authors are grateful for the financial support granted by the Chinese National Science Council. CKC thanks the Mining Research and Service Organization for a research fellowship. YMP thanks the Ministry of Education for a post-graduate fellowship. We thank Dr. C.J. Chang of the Nuclear Energy Reseach Institute for the assistance in obtaining ^{29}Si NMR spectra.

References

1 W.F. Reynolds, J.C. Thompson and A.P.C. Wright, Can. J. Chem., 58 (1980) 419.
2 C.C. Shiau, T.L. Hwang and C.S. Liu, J. Organometal. Chem., 214 (1981) 31.
3 T.L. Hwang, Y.M. Pai and C.S. Liu, J. Amer. Chem. Soc., 102 (1980) 7519.
4 J.C. Thompson and J.L. Margrave, Inorg. Chem., 11 (1972) 913.
5 T.L. Hwang and C.S. Liu, J. Amer. Chem. Soc., 102 (1980) 385—386.
6 A.G. MacDiarmid et al., Private communication, ref. in W.H. Atwell and D.R. Weyenberg, Angew. Chem., Int. Ed. Engl., 8 (1969) 469.
7 P.L. Timms, D.D. Stump, R.A. Kent and J.L. Margrave, J. Amer. Chem. Soc., 88 (1966) 940.
8 D. Seyferth and D.D. Duncan, J. Amer. Chem. Soc., 100 (1978) 7734.
9 C.S. Liu, J.L. Margrave, P.L. Timms and J.C. Thompson, Can. J. Chem., 50 (1972) 459.
10 J.C. Thompson, A.P.G. Wright and W.F. Reynolds, J. Amer. Chem. Soc., 101 (1979) 2236.