conducted with a Philips scintillation counter with a well type thallium-activated sodium iodide crystal. Only the photopeak at 0.77 MeV was counted.

Materials and Solvents. The preparation of **5a**, **5b**, and **5c**[31] and of the anthronylidene derivatives **3a** and **3b**[16] was described previously. The vinyl acetate **8** and its isomer **9** were available from a previous study.[16] 9,10-Anthraquinone, mp 286 °C, was obtained from Ciba. $Et_4N^{82}Br$ was obtained from the Interuniversity Reactor Institute in Delft, The Netherlands. It was prepared by neutron irradiation of Et_4NBr. The n,γ reaction on the natural occurring mixture of $Et_4N^{79}Br$ and $Et_4N^{81}Br$ results in the formation of $Et_4N^{80}Br$ (half-lives 4.5 h and 18 min) and $Et_4N^{82}Br$ (half-life 35.9 h). After appropriate time the amount of $Et_4N^{80}Br$ is negligible. Purification of AcOH was described previously.[31b]

Stability of 9-(α-Bromoanisylidene)anthrone (3a). A mixture of **3a** (2.54 g, 6.5 mM) and tetraethylammonium bromide (14.9 g, 71 mM) in AcOH (20 mL) was refluxed for 6 days. TLC analysis showed only traces of 9,10-anthraquinone.

Stability of 9-Acetoxy-10-anisoylanthracene (9a). (a) A mixture of **9a** (20 mg, 0.07 mM) and sodium acetate (100 mg, 1.22 mM) in AcOH (15 mL) was refluxed for 12 days. TLC on a silica plate showed only the unreacted **9a** up to 11 days, but traces of 9,10-anthraquinone were observed after 12 days.

(b) A mixture of **9a** (20 mg, 0.07 mM), sodium acetate (100 mg, 1.22 mM), and tetraethylammonium bromide (256 mg, 1.22 mM) in AcOH (15 ml) was refluxed for 3 days. TLC on a silica plate showed the formation of >50% 9,10-anthraquinone which was identical with an authentic sample.

Kinetic Procedure. A reaction mixture of 40–50 mL was used for the experiments. With all the compounds except for **3b** no problems were encountered. Erratic kinetic results with the slow reacting **3b** were traced to some evaporation of the solvent after long reaction times and good results were obtained for this compound by using the sealed ampules technique. Because of the slow rate of reaction of **3b**, the product formation for this compound was only followed up to 20% conversion and its exchange up to 40%.

The solvolysis reaction was analyzed by two methods. (a) Analysis by NMR: at regular intervals 5-mL samples were withdrawn from the solution and added to hexane (50 mL); the mixture was washed twice with saturated $NaHCO_3$ solution (50 mL), separated, and dried ($MgSO_4$); the solvent was evaporated, and the remaining solid was dissolved in $CDCl_3$ and analyzed by NMR. (b) Analysis by high-pressure LC: samples of 0.5 or 1.0 mL were withdrawn and added to hexane (10.0 mL) containing a known amount of anisole; after being washed and separated, 20 μL of the hexane solution was injected into an high-pressure LC column. For **3a** a 15-cm Partisil column with 10% THF in hexane as the mobil phase was used. At a flow rate of 1.5 mL/min the retention times were as follows: anisole (internal standard), 1.4 min; 7, 2.2 min; **9a**, 7 min; **8a**, 10.5 min. The retention times for the reaction of **3b** on a 25-cm silica column with 15% THF in hexane as the mobil phase at a flow rate of 2 mL/min were as follows: anisole, 1 min; **3b**, 3.2 min; 7, 3.6 min. For **5a** and **5b** a 15-cm Partisil column with 10% THF in hexane as the mobil phase was used. The retention times were as follows: **5a**, 5.3 min; trianisylvinyl acetate, 9.6 min (at a flow rate of 1.5 mL/min); **5b**, 4.3 min; its corresponding *E*- and *Z*-acetates, 6.2 and 6.7 min (at a flow rate of 1.2 mL/min).

For the exchange reaction 0.5- or 1.0-mL samples were withdrawn at the appropriate times and added to hexane (10.0 mL). After careful washing with water to remove all the inorganic bromide, 5.0 mL of the solution were analyzed for radioactivity by counting the 0.77-MeV peak of the ^{82}Br-γ spectrum with a scintillation counter. In all cases (after correction for the formation of the products indicated) a first-order kinetic behavior of the exchange was observed.[30b]

Acknowledgment. The continuing supply of a gift of $Et_4N^{82}Br$ from the Interuniversity Reactor Institute in Delft, The Netherlands, is gratefully acknowledged. Part of the research in Jerusalem was supported by a grant from the United States-Israel Binational Science Foundation (BSF), Jerusalem, Israel, to which we are indebted.

---

[31] (a) Rappoport, Z.; Gal, A. *J. Am. Chem. Soc.* **1969**, *91*, 5246–5254. (b) Rappoport, Z.; Apeloig, Y. *Ibid.* **1969**, *91*, 6734–6742.

Reactions of Difluorosilylene with Halogen-Substituted Ethylenes. A Reinvestigation of the Reaction Mechanism

Tsai-lih Hwang, Yi-ming Pai, and Chao-shiuan Liu*

Contribution from the Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, Republic of China. *Received March 27, 1980*

Abstract: In supporting our recent discovery of the gas-phase reaction of monomeric difluorosilylene, reactions of SiF_2 with *trans*- and *cis*-difluoroethylene, vinyl chloride, and vinyl fluoride are studied in the gas phase. Compounds from insertion of monomeric SiF_2 into carbon–halogen bonds are the only type of product obtained in these reactions. In order to avoid the complication that might be brought into the case of cocondensation experiments by the gas phase reactions prior to condensation, we carried out well-controlled "alternate layer" experiments for some of the reactions. The results show definitely that some SiF_2 remains monomeric at −196 °C. When the results of the reactions under various experimental conditions are compared, the conclusion shows that the best explanation for the reaction mechanism is the one involving $\cdot(SiF_2)_n\cdot$ diradicals with n = 1,2,3, ··· etc., in which the silirane intermediate can be considered as a special case of $n = 1$.

The reaction mechanism of difluorosilylene has long been controversial.[1,2] Although for a long time we have believed that $\cdot(SiF_2)_n\cdot$ diradicals are mainly responsible for the observed chemistry of difluorosilylene in cocondensation experiments, other possibilities are never ruled out.[3-5] The synthesis and some chemistry of difluorosilirane reported recently by Seyferth suggested an alternative interpretation of the observed chemistry of difluorosilylene,[1] which was backed up by a ^{29}Si NMR study of the $[-CH(CH_3)CH_2SiF_2-]_n$ polymer formed in the reaction of SiF_2 with propene.[6]

In a recent communication[7] we have demonstrated that under proper conditions monomeric $SiF_2(g)$ can react in reasonably good yield with 1,3-butadiene in the gas phase. Because the center of the controversy lies on whether $\cdot(SiF_2)_n\cdot$ diradicals are involved

---

[1] Seyferth, D.; Duncan, D. P. *J. Am. Chem. Soc.* **1978**, *100*, 7734–7736.

[2] Margrave, J. L.; Perry, D. L. *Inorg. Chem.* **1977**, *16*, 1820–1822.

[3] Margrave, J. L.; Wilson, P. W. *Acc. Chem. Res.* **1971**, *4*, 145–152.

[4] Timms, P. L. *Acc. Chem. Res.* **1973**, *6*, 118–123.

[5] Liu, C. S.; Cheng, C. W. *J. Am. Chem. Soc.* **1975**, *97*, 6746–6749.

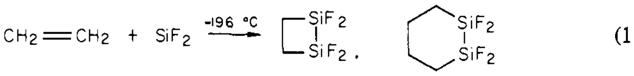
[6] Thompson, J. C.; Wright, A. P. G.; Reynolds, W. F. *J. Am. Chem. Soc.* **1979**, *101*, 2236–2237.

[7] Hwang, T. L.; Liu, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 385–386.

[8] Thompson, J. C.; Margrave, J. L. *Science (Washington, D.C.)* **1967**, *155*, 669–671.

in the cocondensation experiments, the study of the reaction in the gas phase should enable us to obtain information from the conditions under which $\cdot(SiF_2)_n\cdot$ diradicals do not exist. By comparison with the results from cocondensation experiments this information should shed light on the true reaction mechanism of difluorosilylene.[7]

Earlier studies on the reactions of difluorosilylene with ethylene,[9] fluoroethylenes,[10] benzene, and fluorobenzene[11] showed that "addition products" were found in the reactions with ethylene and benzene whereas "insertion products" were obtained with fluoroethylenes and fluorobenzene, for example, eq 1 and 2.



(1)

$$CH_2{=}CHF + SiF_2 \xrightarrow{-196\ °C} CH_2{=}CHSiF_3,\ CH_2{=}CHSiF_2SiF_3 \quad (2)$$

In the case of vinyl chloride, however, both "addition" and "insertion" products were obtained.[12] Although the relative yield of the insertion product $CH_2{=}CHSiF_2Cl$ was low, it clearly indicated the nature of competitive reactivities among various reaction pathways of the reactive intermediates which is characteristic for radical chemistry.[13]

We therefore feel it is time for a reinvestigation of the reactions of difluorosilylene with various halogen-substituted ethylenes in a more systematic and quantitative way; hopefully it would reveal more insight of the reaction mechanism for both insertion and addition reactions in both gas-phase and cocondensation conditions.

Experimental Section

Reactions. All reactions were carried out in a greaseless vacuum system similar to the one used for previous studies of difluorosilylene chemistry described elsewhere.[11] A 6-L bulb was added to the vacuum line and connected at the immediate entrance of a SiF_2/SiF_4 mixture above the furnace so the gas-phase reactions could be carried out in the closed system.[7] A total amount of about 10 mmol of reagent was consummed in each experiment which was executed by repeating 20 runs of the reaction in the closed bulb. Each run was carried out by keeping the reagents in the closed bulb for 25 min, roughly 10 times the half-life of $SiF_2(g)$, so that all SiF_2 was consumed when the gas mixture was finally pumped out of the bulb. No formation of $\cdot(SiF_2)_n\cdot$ was possible under such operations.

Cocondensation experiments for some of the reactions were reinvestigated in a more quantitative manner. In a typical run for the reaction of *trans*-difluoroethylene, for example, 0.798 g of *trans*-$CHF{=}CHF$ and 1.264 g of SiF_4 were used in the reaction while furnace temperature and reaction pressure were kept the same as the conditions used previously (1150 °C and 0.2 torr, respectively.) The molar ratio of the two reagents was 1.02:1.00. Prolonged pumping through a trap kept at -132 °C enabled a clear-cut separation between starting materials and the products. On the basis of the quantity of $CH_2{=}CHF$ used the absolute yield of total product including polymers was found to be 42.8%, among which 0.203 g of volatile product mixture counted for 19.1% yield. For the vinyl fluoride reaction, 0.570 g of $CH_2{=}CHF$ and 1.358 g of SiF_4 (1.00:1.03 molar ratio) were used in the reaction under the same experimental condition. The total yield including polymers was 81.2%. A 0.286-g sample of volatile product mixture was obtained which counted for 14.4% yield by weight.

The "alternate layer" experiments (see Results and Discussion) were carried out by condensing the SiF_2/SiF_4 mixture and the gas reagent alternatively so that no mixing of SiF_2 and the gas reagent was allowed in the gas phase prior to condensing. The condensation of each layer lasted for 20 s and during the process the pressure was kept the same as the partial pressure of each reagent in the previous cocondensation experiments (roughly 0.1 torr). The total quantity of each reagent used in the experiment was also controlled to be the same as that used in a cocondensation experiment so that quantitative comparison of product yields could be made easily.

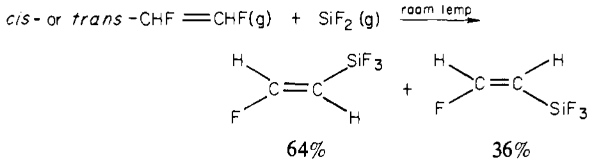
Relative yields of the products were obtained from the intensities of their characteristic peaks in the ^{19}F NMR spectra.[17]

Spectra. A JEOL JMS-100 mass spectrometer, JNM FX-100 NMR spectrometer, and a Perkin-Elmer 580 IR spectrometer were used for product identification. Proton, ^{19}F, and ^{13}C NMR spectra were recorded on the spectrometer operating at 99.60, 93.70, and 25.05 MHz, respectively.

Results and Discussion

Reactions with *cis*- and *trans*-Difluoroethylene. The reactions between difluorosilylene and *cis*- and *trans*-difluoroethylenes carried out by cocondensation experiments have been reported previously.[13] The major products in both reactions include *trans* and *cis* isomers of $CHF{=}CH(SiF_2)_nF$, where n = 1, 2, 3. Both reactions show nonstereospecific insertions with configurational retention over 60% in all cases.

The same reactions are studied in the gas phase in a closed bulb at room temperature for 25 min under conditions of different total pressures and different partial pressures of the reagents (ranging from total pressure 0.5 to 5 torr, and SiF_2/reagent ratio 1:2 to 20:1). The procedures were repeated until all reagents were used up. The results show little dependence on reagent pressure. The only type of product obtained was the compounds formed from insertion of monomeric SiF_2 (eq 3).



(3)

The products were identified unequivocally by means of mass spectrometry and ^1H and ^{19}F NMR spectroscopy. Careful examination showed that no insertion products with n = 2 and 3, $CHF{=}CHSiF_2SiF_3$ and $CHF{=}CHSiF_2SiF_2SiF_3$, respectively, were formed in these reactions. The total yields of both reactions are estimated to be ~15%.

Compared with the results from cocondensation experiments, two major differences are apparent: (i) only monomeric SiF_2 is involved in the reactions in the gas phase whereas $CHF{=}CH(SiF_2)_nF$, n = 1, 2, 3, are involved in the cocondensation reactions (Table I), and (ii) the ratio of relative yields of *trans*-$CHF{=}CHSiF_3$ to *cis*-$CHF{=}CHSiF_3$ is constant in both reactions of *trans*- and *cis*-$CHF{=}CHF$ carried out in the gas phase, which is in sharp contrast to the results of cocondensation reactions (Table II).

For the first point, it appears that in the gas-phase reactions the formation of the products may proceed via an initial attack of the SiF_2 to the carbon-carbon double bond (possibly by formation of a silirane intermediate) followed by rearrangement.[1,13,14] In the case of cocondensation, the formation of $CHF{=}CH(SiF_2)_nF$ (n = 2 and 3 count for nearly 70% of total volatile products) may indicate the involvement of the $\cdot(SiF_2)_n\cdot$ diradical mechanism. However, further clarification is needed.

The second point can be rationalized as follows: a simple estimation from the principle of bond energy additivity shows that under our experimental conditions of the gas phase reactions the initially formed difluorosilirane (should it form at all) would carry too high an energy (~91 kcal/mol) to survive. The reaction product $CHF{=}CHSiF_3$, when initially formed in the gas phase, would carry approximately 95 kcal/mol of energy which is much more than the activation energy of cis/trans isomerization of various substituted ethylenes (50-65 kcal/mol),[16] therefore the

---

(9) Thompson, J. C.; Margrave, J. L.; Timms, P. L. *J. Chem. Soc., Chem. Commun.* **1966**, 566-567.

(10) Orlando, A.; Liu, C. S.; Thompson, J. C. *J. Fluorine Chem.* **1973**, *2*, 103-106.

(11) Timms, P. L.; Stump, D. D.; Kent, R. A; Margrave, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 940-942.

(12) Liu, C. S.; Hwang, T. L. *J. Am. Chem. Soc.* **1979**, *101*, 2996-2999.

(13) Liu, C. S.; Hwang, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 2577-2579.

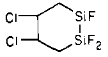
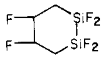
(14) Zeck, O. F.; Su, Y. Y.; Gennaro, G. P.; Teng, Y. N. *J. Am. Chem. Soc.* **1976**, *98*, 3474-3477.

(15) Huheey, J. E. "Inorganic Chemistry", 2nd ed.; Harper and Row: New York, 1978; p 847-848.

(16) Benson, S. W.; O'Neal, H. E. *Data Ser.* (*U.S., Natl. Bur. Stand.*) **1970**, 15.

(17) The data listed in Table II differ considerably from those appearing in ref 13, which were calculated from the product yields after trap-to-trap fractionation. The present results came from the total product mixture without being separated, they are more reliable for quantitative comparison.

Table I. Products from the Reactions with Haloethylenes under Various Conditions and NMR Data of the Products

reaction	conditions		chem Shift[a]			coupling constant, Hz
	cocondensation	gas phase	^{1}H	^{19}F	^{13}C	
trans-CHF=CHF	*trans*- and *cis*- $CHF{=}CH(SiF_2)_nF$, $n = 1, 2, 3$	*trans*- and *cis*- $CHF{=}CHSiF_3$	ref 13			
$CH_2{=}CHCl$	$CH_2{=}CHSiClF_2$ (trace)		ref 12			
	$CHCl{=}CHSiF_2SiF_2CH_2CH_2Cl$		ref 12			
	trans- and *cis*- 		ref 12			
		$CH_2{=}CHSiCl_2F$	5 ~ 6(ABC)	125.6 (t)		$^3J_{HF} \simeq {}^4J_{HF} = 2.8$
		$CH_2{=}CHSiClF_2$	5 ~ 6(ABC)	138.9 (t)		$^3J_{HF} \simeq {}^4J_{HF} = 3.0$
		$CH_2{=}CHSiF_3$	5 ~ 6(ABC)	142.7 (t)		$^3J_{HF} \simeq {}^4J_{HF} = 3.2$
$CH_2{=}CHF$	$CH_2{=}CH(SiF_2)_nF$, $n = 1, 2$		ref 10			
	trans- and *cis*- 		CH_2 1.5 (br) CHF 4.8 (d.d, br)	CF 126 (br) SiF 140 (br)	CH_2 20.3 (m, int 2) 17.8 (m, int 1) CF 91.0 (d.d, int 2) 93.5 (d.d, int 1)	$^2J_{HF} = 48$ (CHF) $^3J_{HF} = 34$ (CHF) $^1J_{CF} = 180$ $^2J_{CF} = 30$
	$(CH_2{=}CH)SiF_2$		6 ~ 7(ABC)	143.8 (m)	CH 128 (t) CH_2 140 (t)	$^2J_{CF} = 20$ $^3J_{CF} = 3.6$
		$CH_2{=}CHSiF_3$	ref 10			

[a] ^{1}H and ^{13}C chemical shifts in δ; ^{19}F chemical shifts in ppm upfield from CCl_3F.

Table II. Relative Yields of the Volatile Products of the Reactions with *cis*- and *trans*-CHF=CHF in Various Reaction Conditions

reaction product	relative yield,[c] %									
	cocondensation				alternate layer				gas phase	
	cis[a]		trans[b]		cis[a]		trans[b]		cis[a]	trans[b]
trans-$CHF{=}CHSiF_3$	5	(77)	18	(62)	6	(78)	18	(64)	64	64
cis-$CHF{=}CHSiF_3$	17		10		21		10		36	36
trans-$CHF{=}CHSi_2F_5$	6	(88)	57	(85)	8	(86)	43	(77)		
cis-$CHF{=}CHSi_2F_5$	44		10		51		13			
trans-$CHF{=}CHSi_3F_7$	2	(93)	6	(86)	2	(86)	13	(81)		
cis-$CHF{=}CHSi_3F_7$	26		1		2		13			

[a] Cis = reaction with *cis*-CHF=CHF. [b] Trans = reaction with *trans*-CHF=CHF. [c] Numbers in the parentheses are the percentage of configuration retention.

constant ratio of trans/cis products actually reflects the thermodynamic distribution according to the energies of the products, namely, *trans*- and *cis*-$CHF{=}CHSiF_3$. It is worth noting that 0.4 kcal/mol of energy difference between the *cis*- and *trans*-$CHF{=}CHSiF_3$ would result in the ratio observed in this experiment.

When the reactions are carried out by cocondensation experiments at −196 °C, the kinetic competition of the radical species among various reaction pathways becomes a controlling factor. The diradical $\dot{C}HF{-}CHF{-}\dot{S}iF_2$ may rearrange to form the product $CHF{=}CHSiF_3$ or rotate about the carbon–carbon single bond and then rearrange to form the geometric isomer. The rotation barrier about the carbon–carbon single bond in such diradical species without important resonance stabilization is in general taken as 6 kcal/mol,[16] and the activation energy for rearrangement process of such diradicals should be of the same order since both trans and cis isomers are observed in each reaction. It is therefore reasonable to observe the various relative yields of trans and cis products in these cocondensation reactions.

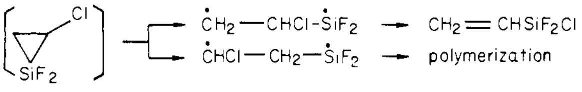
Reactions with Vinyl Chloride. We recently reported the reaction of vinyl chloride with SiF_2 effected by the cocondensation method.[12] The major products from the reaction were found to be *trans*- and *cis*-4,5-dichloro-1,1,2,2-tetrafluoro-1,2-disilacyclohexane and $CHCl{=}CHSiF_2SiF_2CH_2CH_2Cl$, the product from H migration of the diradical intermediate $\dot{C}HCl{-}CH_2{-}SiF_2SiF_2{-}CH_2{-}\dot{C}HCl$. In the reaction carried out in the gas phase, none of these compounds was observed; instead, insertion products were the only volatile products obtained (there was a thin layer of polymeric material formed on the wall of the reaction bulb). The total yield of volatile products based on the quantity of vinyl chloride used was estimated to be less than 10%.

$$CH_2{=}CHCl(g) + SiF_2(g) \xrightarrow{\text{room temp}} \underset{20\%}{CH_2{=}CHSiClF_2},\ \underset{40\%}{CH_2{=}CHSiCl_2F},\ \underset{40\%}{CH_2{=}CHSiF_3}$$

All the compounds were isolated and identified by mass spectrometry and ^{1}H and ^{19}F NMR spectroscopy. The NMR data are summarized in Table I.

$CH_2{=}CHSiCl_2F$ and $CH_2{=}CHSiF_3$ are almost certainly formed via disproportionation of $CH_2{=}CHSiClF_2$ involving halogen exchange. It is of particular interest to note that different experimental conditions of the same reaction lead to a completely different type of reaction products.

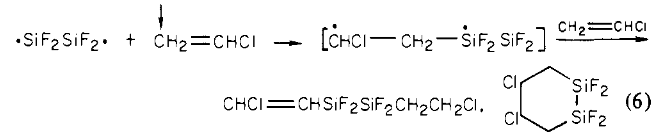
As in the case of the gas-phase reactions of difluoroethylenes described above, only monomeric SiF_2 reacts with vinyl chloride to form the unstable silirane which cleaves and rearranges to the insertion products rapidly. Two ways of cleavage are possible for the hot silirane molecule, only one would lead to the insertion products, the other would probably lead to polymerization (eq 4 and 5).



(4)

(5)

In the case of cocondensation, all major products are formed via "addition" pathways. As pointed out by Seyferth,[1] a silirane intermediate could account for all the products observed. However, a simple rationalization based on the site preference in the initial attack to the unsymmetrically substituted carbon-carbon double bond explains the experimental facts equally well (eq 6).[13]



(6)

trans and cis

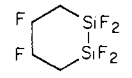
At this moment, more experimental results are required to clarify this point.

A small portion of the polymers formed in the cocondensation experiment (oily material) was soluble in $CDCl_3$ and was studied by ^{29}Si NMR spectroscopy. A large triplet with $J_{Si-F} = 310$ Hz was observed at 21.07 ppm upfield from Me_4Si. It is very similar to the spectrum observed by Thompson et al. for the polymer from the propene/SiF_2 reaction.[6] This suggests that the polymer soluble in $CDCl_3$ consists of $(-CHCl-CH_2-SiF_2-)_n$. Since the major part of the polymers (solid layers) is not very soluble, its composition remains uncertain at this time. However, from the ^{19}F NMR spectrum, where less intense peaks are more detectable than in the ^{29}Si spectrum, the existence of polymers of more complex compositions is obvious.

Reaction with Vinyl Fluoride. The reaction between difluorosilylene and vinyl fluoride in the gas phase gives apparently only one product, $CH_2{=}CHSiF_3$ (eq 7). The yield based on the amount of vinyl fluoride used is estimated to be ≥30%. A thin layer of polymer was found on the wall of the bulb after the reaction.

$$CH_2{=}CHF\ (g) + SiF_2\ (g) \rightarrow CH_2{=}CHSiF_3 \qquad (7)$$

The same reaction carried out by the cocondensation experiment has been studied previously by Thompson et al.[10] Two products, $CH_2{=}CHSiF_3$ and $CH_2{=}CHSiF_2SiF_3$, were reported. For a more detailed comparison with the gas phase reaction, we restudied this reaction in a more quantitative manner under cocondensation conditions. In addition to the two products reported previously two other products are identified, I and II.



I

trans and cis

$$CH_2{=}CH{-}SiF_2{-}CH{=}CH_2 \qquad (7a)$$

II

The two isomers of I were not isolated. They show molecular ion of *m/e* 224 in the mass spectrum. The NMR data are collected in Table I. That both isomers of I are present is evident in the proton-noise decoupled ^{13}C NMR spectrum. Two sets of characteristic peaks both with intensity ratio roughly 2:1 are assigned to the CH_2 and CHF carbons of the two isomers, respectively.

Compound II shows the molecular ion of *m/e* 120 in the mass spectrum. The NMR data are collected in Table I. The multiplet at 143.8 ppm in the ^{19}F NMR spectrum reduces to a singlet when protons are decoupled. The proton-noise decoupled ^{13}C NMR spectrum agrees well with the structural assignment. No C-F signals are observed in the ^{19}F and ^{13}C spectra.

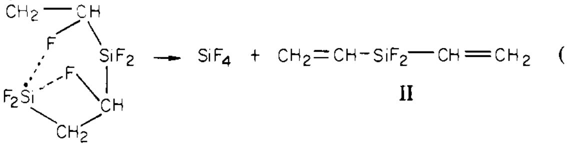
The polymer in this reaction is not very stable thermally. It starts to decompose at above 30 °C. It was therefore desirable to protect the polymer by cooling at 0 °C during the time when volatile products were pumped out for fractionation. On the basis of the quantity of vinyl fluoride used the total yield of volatile products is found to be 15%. The relative yields of $CH_2{=}CHSiF_3$, $CH_2{=}CHSiF_2SiF_3$, II, and I are 18:23:35:24 (Table III).

Table III. Relative Yields of the Volatile Products of the Reaction with Vinyl Fluoride in Various Reaction Conditions

	relative yield, %				
	cocondensation		alternate layer		
reaction product	*a*	*b*	*a*	*b*	gas phase
$CH_2{=}CHSiF_3$	18	57	20	55	100
$CH_2{=}CHSiF_2SiF_3$	23	5	25	6	
$(CH_2{=}CH)_2SiF_2$	35	28	36	30	
I	24	10	19	9	

[a] Polymer was cooled at 0 °C during separation procedures, see text. [b] Products obtained from the pyrolysis of the polymers at 100 °C.

The observation of I is expected. The reason for a product of the structure II is, however, less obvious if viewed from the reaction patterns established previously. Nonetheless we can rationalize it as follows: under the cocondensation conditions diradicals such as $\dot{C}H_2{-}CHF{-}\dot{S}iF_2$ and $\dot{C}H_2{-}CHF{-}SiF_2{-}CHF{-}CH_2{-}\dot{S}iF_2$ may form, the former rearranges to form $CH_2{=}CHSiF_3$ and the latter forms II on elimination of SiF_4 (eq 8).



(8)

II

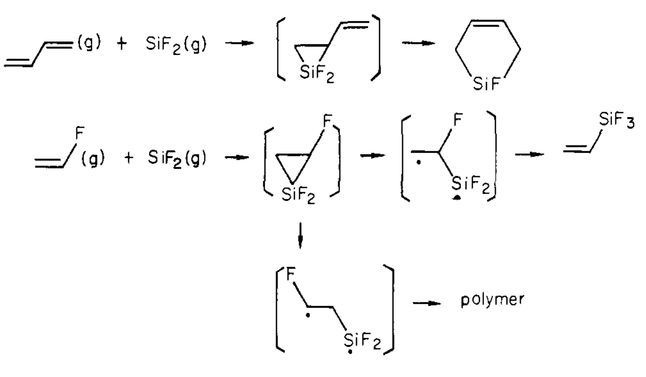
In our previous study of the reaction of difluorosilylene with 1,3-butadiene, in addition to the expected six-membered disilacyclic product, a small amount of 1,1-difluorosilacyclopent-3-ene was observed in the cocondensation experiment.[7] It was suspected that this five-membered monosilacyclic compound, which was the major product in the gas-phase reaction, might have come from the gas-phase reaction prior to condensation. The same suspicion occurs in the present case. The only products in the gas-phase reaction are the products involving monomeric SiF_2. Are these same products observed in the cocondensation experiments actually a result of the gas-phase reaction prior to cocondensation?

To answer this question, the condensation experiment was carried out in an "alternate layer" manner so that no gas mixing was allowed. The alternating condensation procedures were repeated and carefully controlled until the same amount of starting material as was used in a typical cocondensation experiment was consumed.

"Alternate Layer" Experiments. The products of the "alternate layer" reactions between SiF_2 and *trans*-HFC=CHF, vinyl chloride, vinyl fluoride, and 1,3-butadiene are found to be the same as those in the corresponding cocondensation experiments; only the absolute yields are substantially reduced. This is almost certainly due to the poorer mixing of the reagents in such alternate layer experiments. The most important observation from these experiments is the fact that the relative yields of the products do not differ significantly from those of the cocondensation experiments. For example, a carefully controlled "alternate layer" reaction was studied quantitatively for the reaction of vinyl fluoride. The relative yields of $CH_2{=}CHSiF_3$, $CH_2{=}CHSiF_2SiF_3$, $(CH_2{=}CH)_2SiF_2$, and I were found to be 20:25:36:19, very close to those in the cocondensation experiment (Table III). These results indicate that the formation of $CH_2{=}CHSiF_3$ in the gas phase prior to condensation contributes negligibly to the yield of $CH_2{=}CHSiF_3$ in the cocondensation experiment, and the reactions taking place at -196 °C did involve monomeric SiF_2. In fact, reactions with BF_3, H_2S, etc. studied by Margrave[3] have long suggested the involvement of monomeric SiF_2 in the cocondensation reactions; this carefully controlled experiment confirms the point.

Pyrolysis of Polymers. Since the polymer formed in the reaction of vinyl fluoride decomposes under mild condition, a pyrolysis experiment was carried out. The yellowish polymer was under pumping at 0 °C for 20 h before it was heated to 100 °C. Since all products mentioned above were volatile at 0 °C the vapor pressure of the polymer reached below 10 μm after 20 h of pumping. The pyrolysis lasted for 3 h, and the products coming out were condensed immediately at -196 °C. The total yield of

Scheme I



pyrolysis was 14%. After trap-to-trap fractionation, the following products were obtained: SiF_4, Si_2F_6, Si_3F_8, $CH_2{=}CHSiF_3$, $CH_2{=}CHSiF_2SiF_3$, $(CH_2{=}CH)_2SiF_2$, and I. The relative yields of the last four compounds were found to be 57:5:28:10 (Table III).

For comparison the polymer obtained in the "alternate layer" condensation experiment was also subjected to pyrolysis. The same products were obtained in much poorer total yield (5.2%). The ratio of relative yields of $CH_2{=}CHSiF_3$, $CH_2{=}CHSiF_2SiF_3$, $(CH_2{=}CH)_2SiF_2$, and I was found to be 55:6:30:9, almost the same as that of the cocondensation experiment.

The observation of $CH_2{=}CHSiF_2SiF_3$ from pyrolysis of the polymer, though in relatively small quantity, is mechanistically significant. $CH_2{=}CHSiF_2SiF_3$ is a rather volatile compound: it passes through the cold trap at −45 °C under pumping. One therefore tends to believe that the $CH_2{=}CHSiF_2SiF_3$ originating from the cocondensation reaction could not have remained with the polymer after 20 h of pumping at 0 °C. The $CH_2{=}CHSiF_2SiF_3$ observed in this experiment must have come from the decomposition of the polymer during pyrolysis.

Now, if the polymeric material is composed of only one type of repeating unit ($-CHF-CH_2-SiF_2-$), just as the one suggested by Thompson's ^{29}Si NMR study of the polymer from SiF_2/propene reaction, it would be difficult to see how $CH_2{=}CHSiF_2SiF_3$ could have formed through decomposition of such a polymer. In fact, the observation of $CH_2{=}CHSiF_2SiF_3$ in the pyrolysis strongly suggests that units of ($-CH_2-CHF-SiF_2SiF_2-$) are involved in the polymer. This argument in turn supports the involvement of the $\cdot SiF_2SiF_2\cdot$ diradical in the original cocondensation reaction.

Besides, the formation of large quantities of Si_2F_6 and Si_3F_8 may also indicate that the polymers involve segments with more than one SiF_2 unit linked together.

There remains one ambiguity about the formation of the product $CH_2{=}CHSiF_2SiF_3$ (and also $CHF{=}CH(SiF_2)_nF$, $n = 2, 3$, in the reactions of *trans*- and *cis*-$CHF{=}CHF$). Two possible reaction pathways could be considered: (i) successive insertion of SiF_2 units into Si–F bonds, for example

$$CH_2{=}CHF \xrightarrow{SiF_2} CH_2{=}CHSiF_3 \xrightarrow{SiF_2} CH_2{=}CHSiF_2SiF_3$$

and (ii) successive linking of SiF_2 units onto the reaction intermediates such as $\dot{C}HF-CHF-\dot{S}iF_2$ before rearrangement takes place.

Path i is ruled out because in both the gas-phase and cocondensation experiments no further insertion of SiF_2 was observed when pure $CH_2{=}CHSiF_3$ and SiF_2 were mixed. Path ii was not favored because the ratio of configurational retention of the products $CHF{=}CH(SiF_2)_nF$ in the reactions of *trans*- and *cis*-$CHF{=}CHF$ increase with n, the number of SiF_2 units involved in the products, for example, in the reaction of *trans*-$CHF{=}CHF$, 62% for $n = 1$, 85% for $n = 2$, and 86% for $n = 3$ (Table II). If reactions occurred according to (ii), one would expect the order of the retention ratio to be reversed.

On the other hand, if the products $CHF{=}CH(SiF_2)_nF$ are formed through direct attack to the carbon–carbon double bond by $\cdot(SiF_2)_n\cdot$ diradicals, the intermediates $\dot{C}HF-CH(\dot{S}iF_2)_nF$ find a facile path for F migration via either a four-centered transition state (for $n = 2$) or a five-centered transition state (for $n = 3$).

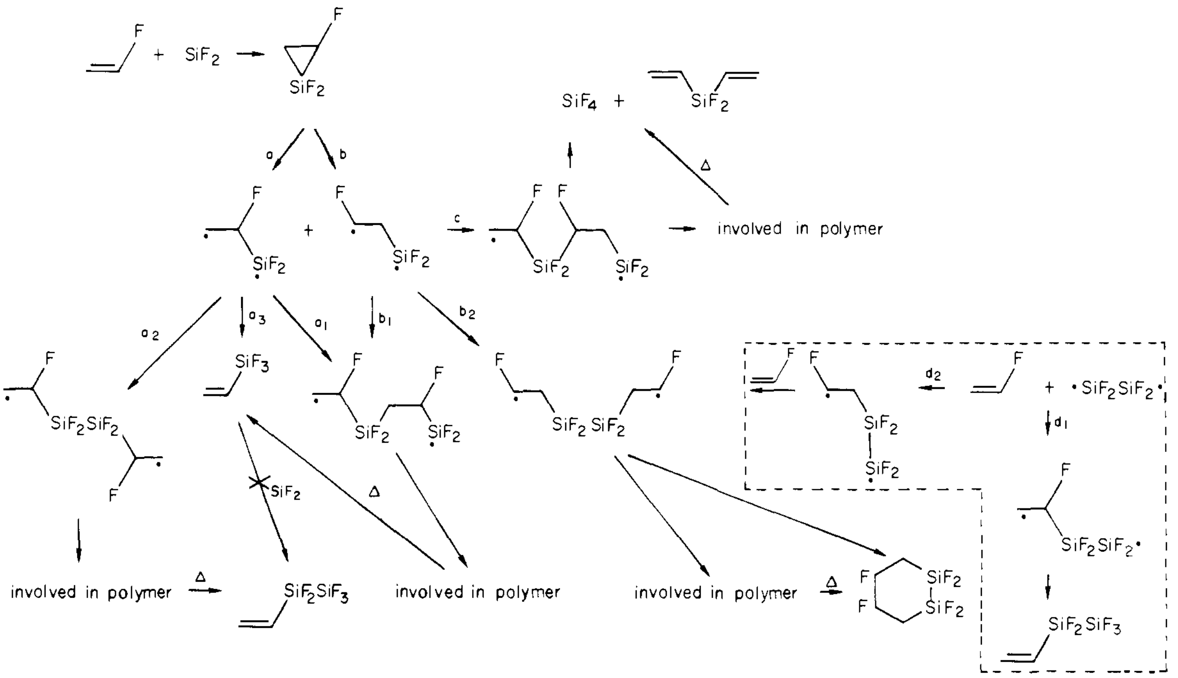
$$SiF_2 + CHF{=}CHF \xrightarrow{-196\ °C} [\cdot(SiF_2)_n\cdot + CHF{=}CHF] \rightarrow CHF{=}CH(SiF_2)_nF \qquad n = 2, 3$$

The Reaction Mechanism. The reactions of SiF_2 with olefins in the gas phase seem rather simple. Difluorosilylene behaves quite similarly to the chemistry of its carbon analogue, carbene. The initial attack of SiF_2 to the carbon–carbon double bond is followed by rearrangement whenever possible. Otherwise it may lead to polymerization. For example, see Scheme I.

The reactions in cocondensation conditions are much more complicated. If silirane does exist as an intermediate, for example, in the case of vinyl fluoride, Scheme II can be proposed.

Paths a and b are the two ways of cleavage of the silirane. Path a_3 results in the products $CH_2{=}CHSiF_3$. Paths a_1, a_2 and b_1, b_2 lead to all possible dimerizations of the diradicals from ring

Scheme II



opening, respectively, which are in turn involved in polymerization. In the case of b_2, the ring closure path may lead to the product disilacyclohexane. All other products from pyrolysis of the polymers are verified experimentally. Path c represents the other possible pathway, the link of the two different radicals from ring opening of the silirane. This path leads to the formation of $(CH_2{=}CH)_2SiF_2$. Although it seems conceivable to obtain $CH_2{=}CHSiF_2SiF_3$ from the polymer pyrolysis, the observation of this compound in the cocondensation reaction can not be explained without raising more skeptical assumptions in this reaction scheme based solely on the silirane intermediate. On the other hand, if the $\cdot SiF_2SiF_2\cdot$ diradical is involved, the formation of $CH_2{=}CHSiF_2SiF_3$ becomes straightforward.

On the basis of argument of the different types of products of each reaction under various experimental conditions (Table I), and the fact that the configuration retentions increase with n in $CHF{=}CH(SiF_2)_nF$ (Table II), the involvement of $\cdot SiF_2SiF_2\cdot$ diradical in the cocondensation reactions is evident. Besides, there have been a number of physical evidences for the existence of $\cdot(SiF_2)_n\cdot$ demonstrated spectroscopically by Margrave's earlier works.[3,4] We therefore add the reaction paths inside the dashed lines into the scheme.

Since our "alternate layer" experiments clearly confirm that some SiF_2 remain monomeric at −196 °C, the silirane mechanism can not be ruled out. The observation of $(CH_2{=}CH)_2SiF_2$ in the vinyl fluoride reaction further augments its plausibility. The silirane mechanism may account for most of the experimental results so far obtained; however, it seems insufficient. In fact, the silirane intermediate may be considered as a special case in the $\cdot(SiF_2)_n\cdot$ homologues with $n = 1$. At this point, we feel that the "difference" between these two mechanisms has been taken too literally and overemphasized. While the detailed reaction mechanism (such as to what extent each mechanism contributes) may vary from reaction to reaction, we tend to conclude that both are involved in the cocondensation experiments in general.[18]

If so, one most important question yet to be answered in the chemistry of SiF_2 is the spin state of the monomeric SiF_2 generated by the thermal reduction method. The formation of silirane as an initial step in these reactions is consistent with the chemistry of singlet SiF_2, which is in agreement with the absence of ESR signal in Margrave's earlier work.[19] Besides, an ab initio calculation also showed that SiF_2 had a singlet ground state.[20] On the other hand, a number of chemical observations have suggested the participation of triplet SiF_2 in some reactions.[21] It is obvious that more work on this point is required to clarify this basic confusion in the chemistry of difluorosilylene.

Acknowledgment. The financial support to this work by the Chinese National Science Council is gratefully acknowledged. T.L.H. thanks the Institute of Nuclear Energy Research for a research fellowship. Y.M.P. thanks the Ministry of Education for a post graduate fellowship.

---

(18) A mechanism involving the direct attack of $\cdot(SiF_2)_n\cdot$ to the CF bonds is seldomly discussed but not ruled out experimentally.

(19) Hopkins, H. P.; Thompson, J. C.; Margrave, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 901–902.

(20) Wirsam, B. *Chem. Phys. Lett.* **1973**, *22*, 360–363.

(21) Chernyshev, E. A.; Komalenkova, N. G.; Bashkirova, S. A. *Russ. Chem. Rev.* **1976**, *45*, 913–930. We also observed that in the study of SiF_2-induced polymerization of isonitriles, trace amounts of oxygen would greatly inhibit the polymerization reactions.

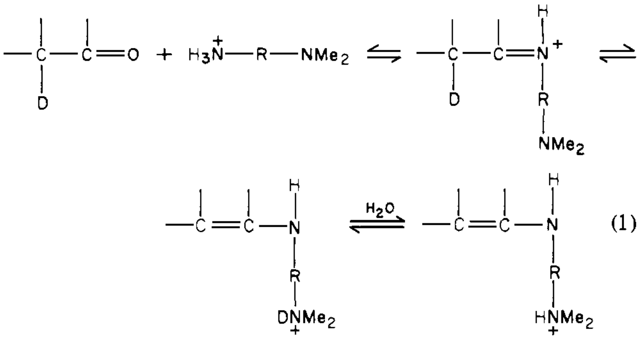
Stereoselective Bifunctional Catalysis of the Dedeuteration of 3-Pentanone-*2,2,4,4-d*$_4$[1]

Jack Hine* and James P. Zeigler

Contribution from the Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210. *Received May 7, 1980*

Abstract: The dedeuteration of 3-pentanone-*2,2,4,4-d*$_4$ was studied in the presence of perchloric acid, sodium hydroxide, and four amines of the type RCH_2NMe_2. The Brønsted β for the amines is 0.56. The monoprotonated forms of both *N*,*N*-dimethyl-1,3-propanediamine and *N*,*N*,2,2-tetramethyl-1,3-propanediamine are bifunctional catalysts for the dedeuteration. Their primary amino group transforms the ketone to an iminium ion from which the tertiary amino group removes a deuteron internally. The monoprotonated form of the chiral catalyst **1** is a very effective bifunctional catalyst and it acts stereoselectively. The pro-*S* deuterons of the ketone are removed more rapidly than the pro-*S* deuterons, by as much as 70-fold. Partially dedeuterated ketone containing more than 80% of the dideuterio species was isolated and found to be optically active, with a positive Cotton effect. Unlike cyclopentanone, which was studied previously, 3-pentanone is dedeuterated less stereoselectively below pH 7 than between pH 8 and 9. The reasons for this are discussed.

Previous studies showed that, in the presence of certain primary–tertiary diamines, α-hydrogen atoms of aldehydes and ketones are exchanged with those of the solvent (water) by a mechanism shown in part in eq 1.[2-5] In the presence of the chiral catalyst (1*R*,2*S*,3*R*,4*R*)-3-[(dimethylamino)methyl]-1,7,7-trimethyl-2-norbornanamine (**1**) the dedeuteration of cyclopentanone-*2,2,5,5-d*$_4$ is highly stereoselective.[1b,5,6]



$$\mathrm{-\underset{D}{\underset{|}{\overset{|}{C}}}-\overset{|}{C}{=}O + H_3\overset{+}{N}-R-NMe_2 \rightleftharpoons -\underset{D}{\underset{|}{\overset{|}{C}}}-\overset{|}{C}{=}\overset{H}{\overset{|}{N^+}}-R-NMe_2 \rightleftharpoons -\overset{|}{C}{=}\overset{|}{C}-\overset{H}{\overset{|}{N}}-R-D\overset{+}{N}Me_2 \underset{}{\xrightleftharpoons{H_2O}} -\overset{|}{C}{=}\overset{|}{C}-\overset{H}{\overset{|}{N}}-R-H\overset{+}{N}Me_2} \quad (1)$$

---

(1) (a) Research supported in part by Grant GM 18593 from the National Institute of General Medical Sciences, Part 21 in the series "Catalysis of α-Hydrogen Exchange". (b) For part 20 see Hine, J.; Li, W.-S.; Zeigler, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 4403–9. (c) Abstracted in part from the Ph.D. Dissertation of James P. Zeigler, The Ohio State University, Columbus, OH, 1978.

(2) Hine, J.; Cholod, M. S.; Jensen, J. H. *J. Am. Chem. Soc.* **1971**, *93*, 2321–2.

(3) Hine, J.; Lynn, J. L., Jr.; Jensen, J. H.; Schmalstieg, F. C. *J. Am. Chem. Soc.* **1973**, *95*, 1577–81.

(4) Hine, J.; Cholod, M. S.; King, R. A. *J. Am. Chem. Soc.* **1974**, *96*, 835–45.

(5) Hine, J. *Acc. Chem. Res.* **1978**, *11*, 1–7.

(6) Hine, J.; Li, W.-S. *J. Am. Chem. Soc.* **1975**, *97*, 3550–1.

0002-7863/80/1502-7524$01.00/0