Journal of Organometallic Chemistry, 235 (1982) 7—15
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CYCLOADDITION REACTIONS OF 1,1,2,2-TETRAFLUORO-1,2-DISILACYCLOBUTENE WITH ALDEHYDES AND KETONES

CHUNG-PING CHIN and CHAO-SHIUAN LIU *
Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan (Republic of China)

(Received January 16th, 1982; in revised form March 16th, 1982)

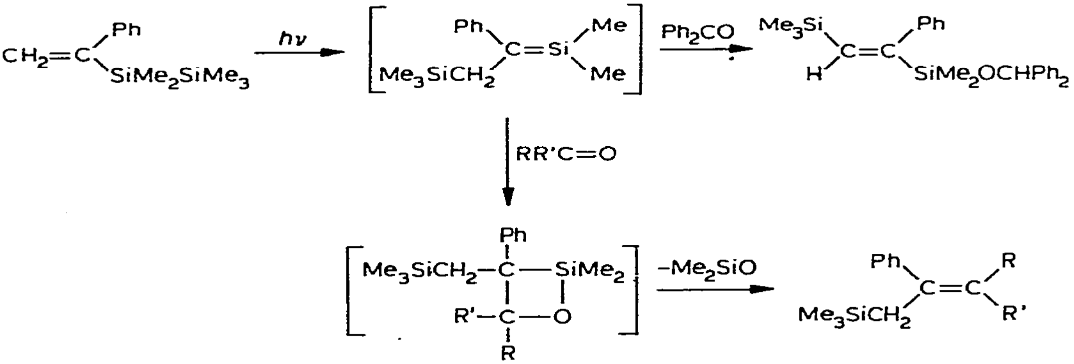
Summary

The reactions of 1,1,2,2-tetrafluoro-1,2-disilacyclobutene with aldehydes and ketones are studied at 0—5°C. The formation of the products found is rationalized in terms of an initial attack by the carbonyl oxygen on one of the two silicon atoms, which assists the cleavage of the Si—Si bond to form a diradical intermediate, followed by either ring closure or hydrogen abstraction.

Introduction

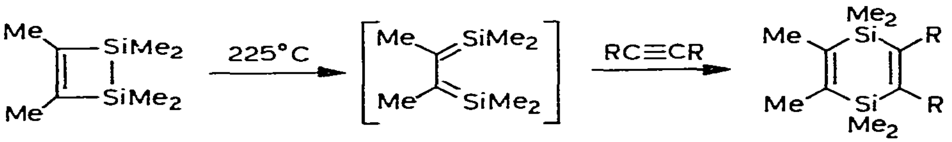
In recent years [1,2], vinyldisilanes have been a much studied system in which 1,2-disilacyclobutenes represent a special class. Not only do the electronic spectra indicate the involvement of p_π—d_π and π—σ interactions in these compounds, but the chemistry of these compounds suggests the existence of Si=C intermediacy [1—3]. The recent direct evidence for stable silaethenes presented by Brook's group certainly adds more support to this idea [4,5].

Under photochemical conditions, the vinyldisilane has been proposed to undergo a 1,3-sigmatropic shift to form the Si=C intermediate which is trapped by various reagents. In the case of ketone reactions, for example [6]:

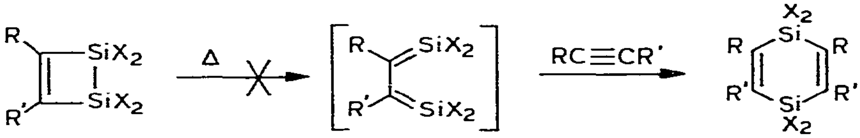


0022-328X/82/0000—0000/$02.75

A Si=C intermediate has also been proposed to interpret the chemistry of 1,2-disilacyclobutenes under thermochemical conditions, for example [7]:

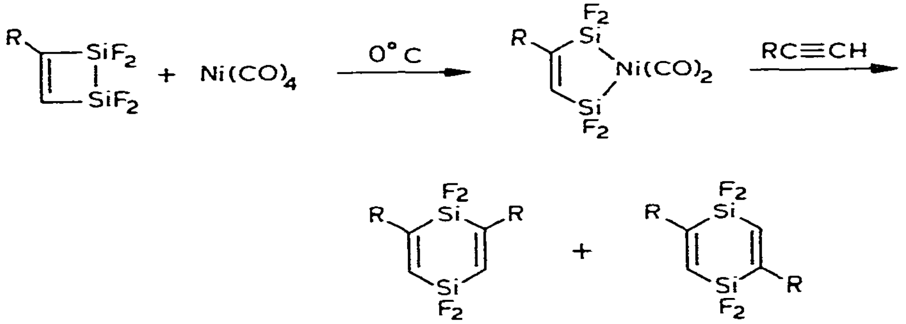


However, in the case of 1,1,2,2-tetrahalo-1,2-disilacyclobutenes, the analogous reactions did not yield the expected 1,4-disilacyclohexadienes [8,9].



X = Cl, F

In the case of 1,1,2,2-tetrafluoro-1,2-disilacyclobutene, the reaction proceeds only in the presence of $Ni(CO)_4$ as catalyst [9].



In fact, all our attempts at trapping the 1,1,4,4-tetrafluoro-1,4-disilabutadiene intermediate in both photochemical and thermochemical conditions have only resulted in the formation of disilametallocycles, whose structure has been determined by single crystal X-ray diffraction [10,11]. This leads us to a reconsideration of the reaction intermediacy of 1,1,2,2-tetrafluoro-1,2-disilacyclobutenes, particularly under thermal reaction conditions.

In view of the charge distribution in the silaethenes, $>C=SiF_2$ is probably the least stable because of the very strong electron-withdrawing fluorine atoms attached to the silicon atom. We therefore were interested in how 1,1,2,2-tetrafluoro-1,2-disilacyclobutenes behaved towards carbonyl compounds.

Experimental

Preparation of 3-tert-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene

3-Tert-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene (I) was prepared by treating difluorosilylene with tert-butyl acetylene under cocondensation condition. Apparatus and reaction conditions similar to those previously described were employed for the reaction [12].

Reactions of 3-tert-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene

The reactions of compound I with aldehydes and ketones were carried out in n-pentane in an evacuated reaction tube at 0—5°C. In a typical reaction, there was placed 0.75 g (3.5 mmol) of compound I in 20 ml of n-pentane in a reaction tube with a fine stopcock. To this was added slowly an equimolar amount of carbonyl compound (also in n-pentane). No air was allowed. The reaction mixture was stirred for 3 h and was then pumped into a vacuum line for trap-to-trap fractionation.

For the reaction of acetaldehyde the volatile products were separated from the unreacted acetaldehyde by pumping through a trap at —25°C. A small quantity of yellowish polymeric material was left in the reaction tube. The products collected at —25°C accounted for 70% yield based on compound I. Two colorless liquid compounds, IA and IB, in this fraction were identified but not separated.

For the reaction of propionaldehyde the volatile products were colorless liquids and were collected at —25°C under pumping. Small amounts of viscous polymeric products left in the reaction tube were not identified. The fraction collected at —25°C contained IIA and IIB, with 72% total yield.

For the reaction of benzaldehyde the solvent and excess reactants were pumped out at room temperature. The products were viscous yellowish green liquids with low volatility. Two compounds IIIA and IIIB were obtained. The total yield was estimated to be 68% based on I.

For the reaction of acetone all products were separated from the excess reactants and collected at —15°C under pumping. The total yield was 74%. Three colorless liquid compounds were obtained and identified as IVA, IVB and VA.

Spectra

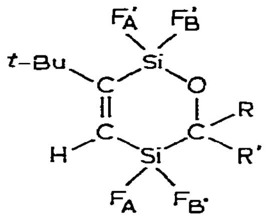
The ^{1}H and ^{19}F NMR spectra were obtained on a JNM FX-100 NMR spectrometer, operating at 99.6 and 93.7 MHz, respectively. In all cases $CDCl_3$ was used as the solvent, with TMS and CCl_3F as internal references for ^{1}H and ^{19}F spectra, respectively. The mass spectra were obtained on a JMS-100 mass spectrometer at 12 eV. The IR spectra were recorded on a Perkin Elmer 580 spectrometer. Samples were measured as films prepared under an inert atmosphere.

Results and discussion

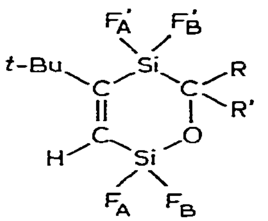
The products from the four reactions and their IR data are listed in Table 1. The mass spectral data are summarized in Table 2. The ^{1}H and ^{19}F NMR data are collected in Tables 3 and 4.

These spectral data unequivocally show that the products are of the structures given below.

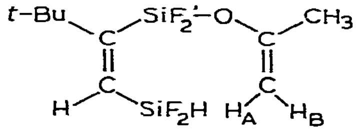
For the structure of the six-membered ring compounds the most informative results came from the ^{19}F NMR spectra. When protons are noise decoupled, all SiF_2 units show either A_2 or AB or AX patterns. From the relative intensities of these spectra it is clear that the four sets of A_2/AB/AX spectra belong to two different compounds. The differentiation between the two isomers is achieved



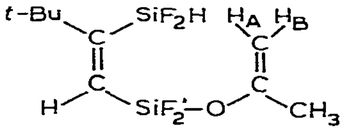
(IA, $R = H$, $R' = CH_3$;
IIA, $R = H$, $R' = C_2H_5$;
IIIA, $R = H$, $R' = C_6H_5$;
VA, $R = CH_3$, $R' = CH_3$)



(IB, $R = H$, $R' = CH_3$;
IIB, $R = H$, $R' = C_2H_5$;
IIIB, $R = H$, $R' = C_6H_5$)



(IVA)



(IVB)

when the H—F coupling constants are determined. For example, in the case of the reaction with acetaldehyde, the product with an SiF_2 group which couples with the vinyl and methine protons to give coupling constants of 6 and 5.8 Hz, respectively (Table 3), is believed to be of structure IA. On the other hand, the compound with coupling constants F—H (vinyl) of 8 Hz but F—H (methine) almost zero Hz fits the structure of IB (Table 3).

One interesting feature of the NMR spectra is that the coupling constant between the methine proton and one F in the adjacent SiF_2 group is apparently zero, in spite of being only three bonds apart. This is true for compounds IA, IIA and IIIA. For example, the SiF_2 group adjacent to the methine H in compound IA shows in the ^{19}F NMR spectrum an AB pattern, the lower field half (139.6 ppm) being further split into doublets but the higher field half (143.0 ppm) being split into triplets. When the protons are noise decoupled, all fine structure is removed and a sharp AB pattern results (Fig. 1). The methine H shows in the ^1H NMR spectrum a doublet of quartets which resembles a quintet because of the similar magnitude of the coupling constants. The same phenomenon is observed with compound IIA where the methine H shows a doublet of triplets which resembles a quartet. For compound IIIA, because the coupling between the methine H and the phenyl ring protons is too small to be observed, the methine H shows a sharp doublet. In accord with these observations, the adjacent SiF_2 group of IIIA shows an AB pattern in the ^{19}F NMR spectrum with one half (138.5 ppm) being split into doublets and the other half (140.1 ppm) being split into doublets of doublets.

In the case $R = R' = CH_3$, a different type of products, IVA and IVB, is obtained in addition to the six-membered ring compounds VA. The structure of IVA and IVB is determined on the basis of the following characteristic spectral features: (i) the mass spectrum shows the parent ion at $m/e = 272$, (ii) the IR

(continued on p. 13)

TABLE 1

IR DATA FOR IA(IB), IIA(IIB), IIIA(IIIB) and IVA(IVB, VA) [a]

	IA(IB)	IIA(IIB)	IIIA(IIIB)	(VA(IVB, VA)
ν(C—H)	2968s	2958s	3050m	3118w
	2872m	2860m	2160s	2965s
			2860s	2874m
ν(Si—H)				2246m
ν(C=C)	1544m	1540m	1600m	1654s
			1548m	1556m
δ(C—H)	1398m	1395w	1393w	1395w
	1375m	1376w	1369s	1375s
	1370m	1368m	1322s	1369s
ν(C—O)	1125s	1120m	1088s	1260s
	1102s	1080s		
ν(Si—O)	1070s	1050s	1068s	1080s
ν(Si—F)	925s	905s	912s	928s
	865s	860s	870s	878s

[a] IA(IB): sample consisting of 76% IA and 24% IB.
IIA(IIB): sample consisting of 93% IIA and 7% IIB.
IIIA(IIIB): sample consisting of 92% IIIA and 8% IIIB.
IVA(IVB, VA): sample consisting of 74% IVA, 15% IVB and 11% VA.

TABLE 2

MASS SPECTRAL DATA FOR IA(IB), IIA(IIB), IIIA(IIIB) and IVA(IVB, VA)

Ion	m/e	Abundance [a]			
		IA(IB)	IIA(IIB)	IIIA(IIIB)	IVA(IVB, VA)
$C_3H_6^+$	42	9	100		100
$C_3H_7^+$	43			10	
$C_4H_9^+$	57	79	71	59	72
$C_5H_7^+$	67	22	18		15
$C_5H_9^+$	69	13	14		18
$C_5H_{10}^+$	70			4	
$C_6H_9^+$	81	26	14		
$C_6H_{10}^+$	82				21
$C_6H_{11}^+$	83				
$C_7H_6^+$	90			100	
$C_7H_5O^+$	105			14	
$C_3H_5OSiF_2^+$	123				10
$C_4H_3OSiF_2^+$	133				8
$C_5H_6OSiF_2^+$	148				14
$C_3H_3OSi_2F_4^+$	187	12	15		
$C_4H_6OSi_2F_4^+$	202	10	6		
$C_6H_{11}Si_2F_4^+$	215	100	71	3	56
$C_6H_{10}OSi_2F_4^+$	230	31	23	2	12
$C_7H_{11}OSi_2F_4^+$	243	15			
$C_8H_{13}OSi_2F_4^+$	257		4		
$C_8H_{14}OSi_2F_4^+$	258	85			
$C_9H_7OSi_2F_4^+$	263			11	
$C_9H_{16}OSi_2F_4^+$	272		17		
$C_{12}H_{13}OSi_2F_4^+$	305			5	
$C_{13}H_{16}OSi_2F_4^+$	320			27	

[a] Same samples as in Table 1.

TABLE 3

NMR DATA FOR COMPOUNDS IA, IB, IIA, IIB, IIIA, IIIB AND VA [a]

Compound	t-Bu	H	R	R′	F_A,F_B	$F'_AF'_B$	Coupling constants (Hz)
IA	1.17(s)	6.56(m)	H, 4.18(d,q)	CH_3, 1.50(d)	139.6 143.0 (AB^{d}_{t})	137.7 138.3 (AB^{u}_{d})	$J(F_A-F_B) = 23$, $J(F'_A-F'_B) = 50$, $J(H-F_A) = 6$ $J(H-F_B) = 5.8$, $J(H-F'_A) = 3.6$, $J(H-F'_B) = 3.6$ $J(R-F_A) = 0$, $J(R-F_B) = 5.8$, $J(R-R') = 8$
IB					132.5 133.3 (AB,d)	121.5 143.8 (AX,d)	$J(F_A-F_B) = 58$, $J(F'_A-F'_B) = 25$, $J(H-F_A) = 8$ $J(H-F_B) = 8$, $J(R-F'_A) = 8$, $J(R-F'_B) = 1.8$
IIA	1.19(s)	6.57(m)	H, 3.94(d,t)	CH_2 1.85(q^n) CH_3 1.07(t)	137.6 141.7 (AB^{d}_{t})	138.3 138.3 (A_2,d)	$J(F_A-F_B) = 22$, $J(H-F_A) = 5.8$, $J(H-F_B) = 6.2$ $J(H-F'_A) = 2.8$, $J(H-F'_B) = 2.8$, $J(R-F_B) = 6.2$ $J(R-R') = 7.1$
IIB					133.8 133.8 (A_2,d)	119.4 143.3 (AX,d)	$J(F'_A-F'_B) = 22$, $J(H-F_A) = 8$, $J(H-F_B) = 8$ $J(R-F'_A) = 8$, $J(R-F'_B) = 2$
IIIA	1.12(s)	6.55(m)	H, 5.19(d)	C_6H_5, 7.25(c)	138.5 140.1 (AB^{d}_{d},d)	136.1 139.1 (AB^{u}_{d})	$J(F_A-F_B) = 20$, $J(F'_A-F'_B) = 57$, $J(H-F_A) = 6.3$ $J(H-F_B) = 4.8$, $J(H-F'_A) = 3.2$, $J(H-F'_B) = 3.2$ $J(R-F_B) = 10$
IIIB					131.1 134.6 (AB,d)	142.6 145.7 (AB^{u}_{d})	$J(F_A-F_B) = 60$, $J(F'_A-F'_B) = 27$, $J(H-F_A) = 7.1$ $J(H-F_B) = 6.0$, $J(R-F'_A) = 7$, $J(R-F'_B) = 11$
VA	1.18(s)	6.45(m)	CH_3, 1.44(s)	CH_3, 1.44(s)	143.5 143.5 (A_2,d)	136.6 136.6 (A_2,d)	$J(H-F_A) = 7.2$, $J(H-F_B) = 7.2$ $J(H-F'_A) = 3.1$, $J(H-F'_B) = 3.1$

[a] Proton chemical shifts in δ, ^{19}F chemical shifts in ppm upfield from CCl_3F as internal reference. u = unresolved, c = complex.

TABLE 4

NMR DATA FOR COMPOUNDS IVA AND IVB [a]

Compound	t-Btu	H	CH_3	H_A,H_B	SiH	F	F′	coupling constants (Hz)
IVA	1.18(s)	6.45(m)	1.86(s)	4.25 (AB) 4.36	5.08(t,t)	135.5(d,m)	132.3(m)	$JF-F') = 4$, $J(H-F) = 4$, $J(H-F') = 6.8$ $^2JSiH-F) = 68$, $^5J(SiH-F) = 4$,
IVB						136.9(d,m)	134.6(m)	$J(F-F') = 4$, $J(H-F) = 4$, $J(H-F') = 6.4$ $^2J(SiH-F) = 68$

[a] Proton chemical shifts in δ, ^{19}F chemical shifts in ppm upfield from CCl_3F as internal reference.

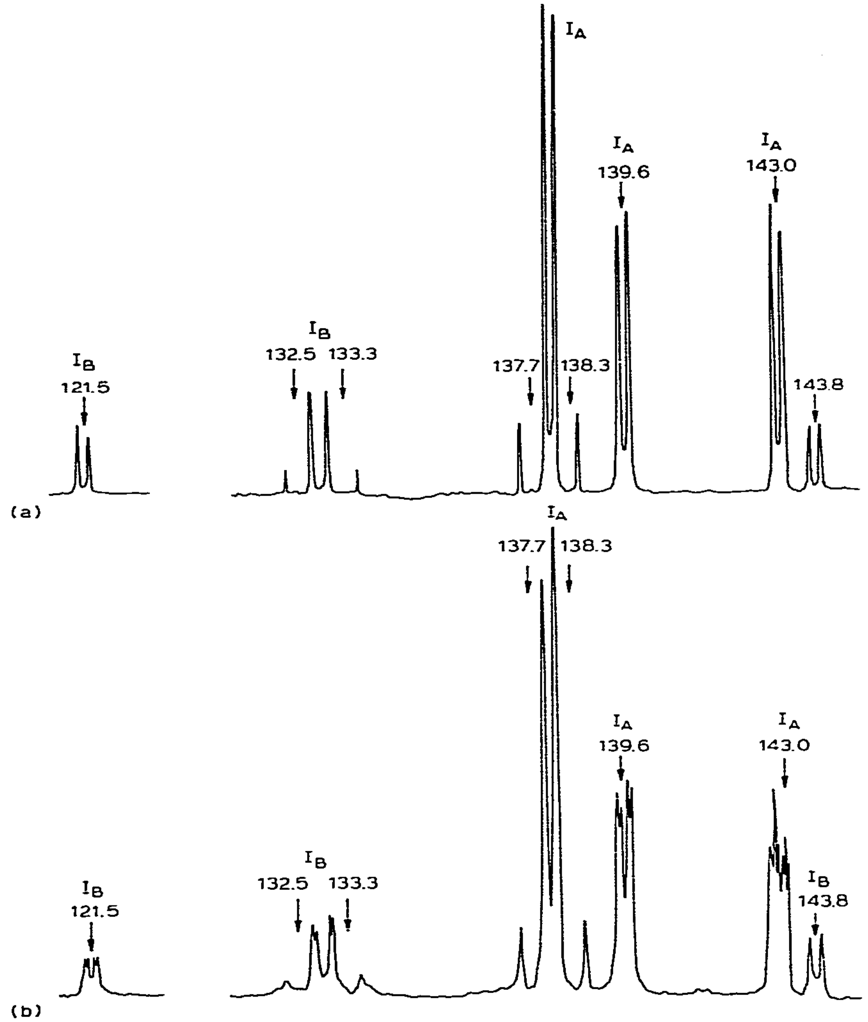


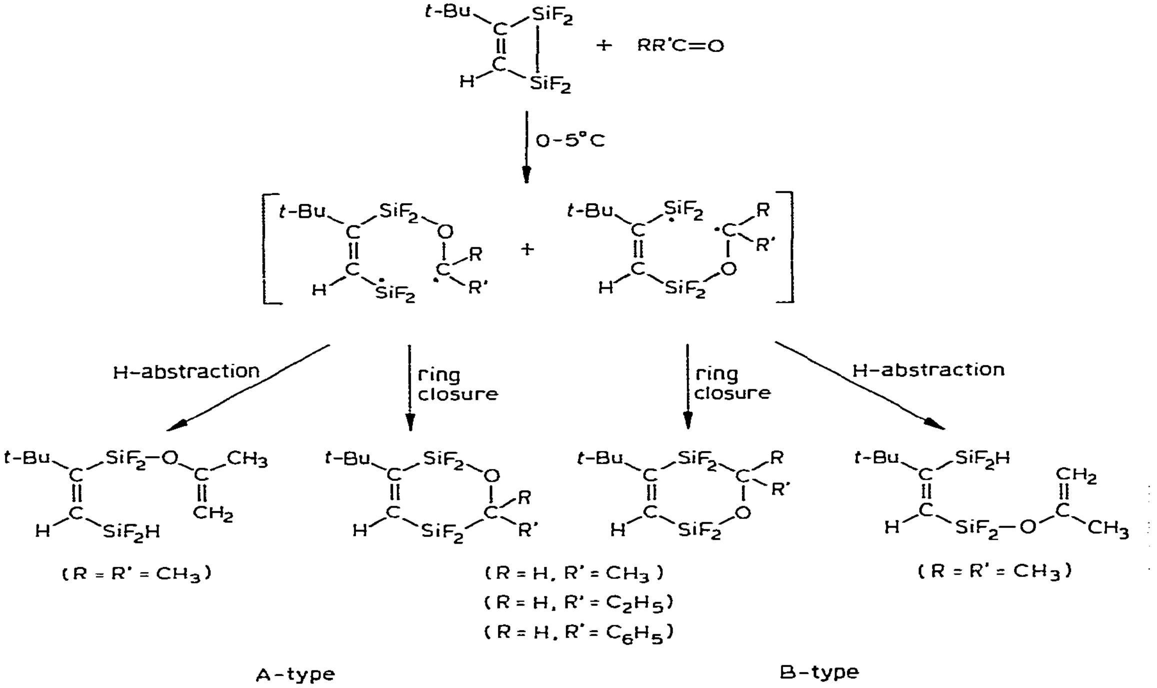
Fig. 1. (a) Proton-decoupled ^{19}F NMR spectrum of a mixture of IA and IB. (b) ^{19}F NMR spectrum of IA and IB.

spectrum shows a sharp absorption at 2246 cm^{-1}, characteristic of Si—H stretching, (iii) the ^1H spectrum shows a triplet ($J = 68$ Hz) which is characteristic of an $—SiF_2H$ moiety, and an AB pattern for the vinyl protons centering at δ 4.31 ppm, a chemical shift typical of a $CH_2{=}CR—O—$ moiety, and, (iv) the ^{19}F NMR spectrum shows two sets of similar spectra, each set consists of a multiplet and a doublet ($J = 68$ Hz) of multiplets. On proton-noise decoupling, the large doublet coupling of 68 Hz disappears and becomes one triplet, as a result of the long-range F—F coupling by the other SiF_2 group. The relative abundance of IVA and IVB is estimated to be 5:1. The complete NMR spectral data of IVA and IVB are summarized in Table 4.

Besides compounds IVA and IVB, a small quantity of the product of six-membered ring structure, VA, is also present in this fraction. Compound VA shows two doublets at 136.6 and 143.5 ppm in the ^{19}F NMR spectrum. On proton-noise decoupling, the two doublets reduce to singlets. No evidence for the existence of VB, the other isomer of the six-membered ring, is obtained.

The existence of compounds IVA and IVB is considered as a strong indication of a reaction mechanism involving radical intermediates. The thermal reactions studied in this work can be rationalized with a simple scheme (Scheme 1).

SCHEME 1



A full analysis of the proton-decoupled ^{19}F NMR spectrum of I, an AA'XX' pattern, shows that the fluorines on the SiF_2 group closer to the tert-butyl group (chemical shift 129.70 ppm) are more shielded than the other SiF_2 group (chemical shift 125.01 ppm); this may imply that the Si atom closer to the tert-butyl group has a stronger affinity for the carbonyl oxygen. The strong affinity between the oxygen and the silicon atom may assist the cleavage of the Si—Si bond and the formation of the diradical intermediate. This is in agreement with the observed relative yields of the isomers of the products (Table 1). The steric interaction between the R and R' groups and the bulky tert-butyl group may also enhance the selectivity. The reason why hydrogen abstraction occurred in the reaction with acetone but not in the reactions with aldehydes is not at all certain. It is possible that steric effects would keep the alkyl groups of the aldehydes away from the $-\dot{S}iF_2$ radical, so that ring closure proceeds more easily. Some reactions designed to provide information in this respect are now under investigation.

It is worth mentioning that when the reactions are viewed as being initiated by nucleophilic attack of the carbonyl oxygen at one of the silicon atoms, then a mechanism involving a zwitterionic intermediate seems equally plausible. With the experimental evidence presently available, we cannot distinguish between these two mechanisms.

In view of the unfavored situation of the silaethene with two fluorines attached to the silicon, it seems to us that as far as the reactions of 1,1,2,2-tetrafluoro-1,2-disilacyclobutenes are concerned, there is no compelling need to propose a 1,4-disilabutadiene intermediate to account for the experimental results.

Acknowledgement

The authors are grateful for the financial support to this work by the Chinese National Science Council. One of us (C.P.C.) thanks the Chinese Army Academy for a research fellowship.

References

1 (a) M. Ishikawa, T. Fuchikami, and M. Kumada, J. Organometal. Chem., 117 (1976) C58.
(b) T.J. Barton, W.D. Wulff, E.V. Arnold and J. Clardy, J. Amer. Chem. Soc., 101 (1979) 2733.
2 H. Sakurai, Y. Kamiyama and Y.J. Nakadaira, J. Amer. Chem. Soc., 98 (1976) 7424.
3 H. Sakurai and M. Kumada, Bull. Chem. Soc. Jpn., 37 (1964) 1894.
4 A.G. Brook, J.W. Harris, J. Lennon and M. Sheikh, J. Amer. Chem. Soc., 101 (1979) 83.
5 A.G. Brook, S.C. Nyburg, W.F. Reynolds, Y.C. Poon, Y.M.'Chang and J.S. Lee and J.-P. Picard, J. Amer. Chem. Soc., 101 (1979) 6750.
6 M. Ishikawa, T. Fuchikami, and M. Kumada, J. Organometal. Chem., 149 (1978) 37.
7 T.J. Barton and T.A. Kilgour, J. Amer. Chem. Soc., 98 (1976) 7746.
8 S.A. Bashkirova, E.A. Chernyshev, and N.G. Komalenkova, First All-Union Symposium on Structure and Reactivity of Organosilicon Compounds, Irkutsk, Sept. 1977, p. 166.
9 C.S. Liu and C.W. Cheng, J. Amer. Chem. Soc., 97 (1975) 6746.
10 T.H. Sheu, Y. Chi and C.S. Liu, Inorg. Chem., 20 (1981) 199.
11 Y. Chi and C.S. Liu, Inorg. Chem., 20 (1981) 3456.
12 P.L. Timms, R.A. Kent, T.C. Ehlert and J.L. Margrave, J. Amer. Chem. Soc., 87 (1965) 2824.