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

II *. CONJUGATED ALDEHYDES AND STERICALLY HINDERED KETONES

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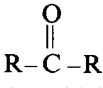
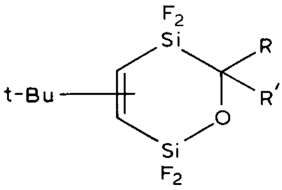
Summary

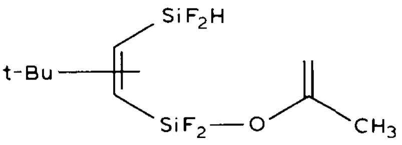
The reactions of 1,1,2,2-tetrafluoro-1,2-disilacyclobutene with benzophenone, pinacolone, acrolein and crotonaldehyde are studied at −30°C. The product formation is best rationalized in terms of an initial attack by the carbonyl oxygen on one of the two silicon atoms, which assists the cleavage of the Si–Si bond to form a diradical intermediate, followed by either ring closure or hydrogen abstraction. The reactions are so chosen to provide information about steric, inductive and resonance effects.

Introduction

Recently, we reported the cycloaddition reactions between 3-tert-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene and a number of simple organic carbonyl compounds,  $R-\overset{\overset{O}{\|}}{C}-R'$, where $R = H$, $R' = CH_3$, C_2H_5, C_6H_5; and $R = R' = CH_3$ [1]. For all the aldehydes, the only type of product formed is the isomers of the six-membered ring compound A. In the case of acetone, however, products resulting from hydrogen abstraction, B, are also obtained.



(A)



(B)

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* For part I see ref. 1.

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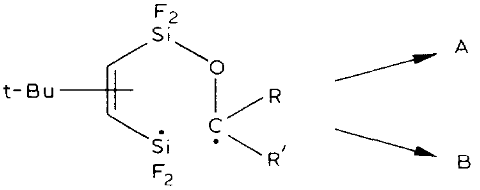
Unlike the reactions between tetramethylvinyldisilanes and carbonyl compounds, in which a Si=C intermediate was postulated [2–5]; the reactions of tetrafluoro-1,2-disilacyclobutene were explained by a mechanism involving diradical intermediacy [1].



In order to strengthen the ground for our proposed mechanism, we chose some more carbonyl compounds for study. Benzophenone and pinacolone were chosen for comparison with the reactions of benzaldehyde and acetone, respectively, and acrolein and crotonaldehyde were chosen for a study of the effect of conjugation.

Experimental

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

This compound was prepared by cocondensation of SiF_2 with tert-butyl acetylene [6].

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

The reactions between the above-obtained 1,2-disilacyclobutene and carbonyl compounds were carried out in n-pentane solutions in an evacuated reaction tube at −30°C. In a typical reaction, there were placed 1.5 g (7 mmol) of the 1,2-disilacyclobutene in 25 ml of pentane in a reaction tube with a fine teflon stopcock. To this was added slowly an equimolar carbonyl compound (also in pentane solution). No air was allowed into the tube. The reaction mixture was kept at −30°C and stirred for 6 h before it was pumped into a vacuum line for trap-to-trap fractionation.

The separation conditions and product yields of the reactions with benzophenone, pinacolone, acrolein, and crotonaldehyde are summarized as follows:

Reactant	Product [a]	Phys [b]	T(°C) [c]	Yield (%) [d]
$(C_6H_5)_2CO$	IA, IB	yellow oil	−5 ~ −15	67
$(t\text{-}C_4H_9)(CH_3)CO$	IIA IIA′, IIB′	colorless oil	−5 ~ −20	70
$CH_2{=}CHCHO$	IIIA	colorless oil	0 ~ −15	72
	IIIC, IIID	colorless liq.	−15 ~ −45	7
$CH_3CH{=}CHCHO$	IVA	colorless oil	0 ~ −18	78

[a] See text. [b] Physical appearance. [c] Collecting temperature. [d] Based on the quantity of the 1,2-disilacyclobutene used.

In all cases the products of types A and B are pairs of structural isomers and were only purified as isomeric mixtures. Attempts to separate them further were not successful because all products were very air sensitive. In each reaction there was a small quantity of non-volatile polymeric product left in the reaction tube, which was not identified.

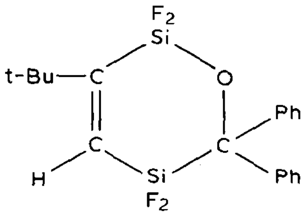
Spectra

The ^{1}H, ^{19}F and ^{13}C NMR spectra were obtained on a JNM FX-100 NMR spectrometer, operating at 99.6, 93.7 and 15.8 MHz, respectively. In all cases $CDCl_3$ was used as the solvent, with TMS and CCl_3F as internal references for ^{1}H/^{13}C and ^{19}F spectra, respectively. The mass spectra were recorded on a JMS-100 mass spectrometer and were measured at 12 eV. The IR spectra were recorded on a Perkin Elmer 580 spectrometer. Samples were measured as films prepared under dry inert atmosphere.

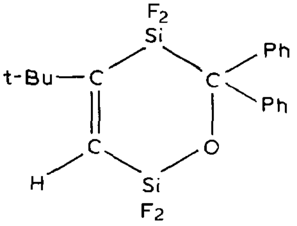
Results and discussion

The IR data of the products from the four reactions are listed in Table 1. The mass spectral data are summarized in Table 2. The NMR data are collected in Tables 3 and 4.

Two isomers of the six-membered ring compound (IA and IB) are the products of the reaction with benzophenone. They show characteristic NMR spectra of the ring which were described previously [1].



(I A)



(I B)

TABLE 1

IR DATA OF IA(IB), IIA′(IIB′), IIIA, IIIC(IIID) AND IVA [a]

	IA(IB)	IIA′(IIB′)	IIIA	IIIC(IIID)	IVA
ν(C–H)	3120w	3075w	2980s	2968s	2965s
	2980s	2965s	2870s	2920m	2880m
	2875m	2880m			
ν(Si–H)		2246m		2242m	
ν(C=C)	1570s	1620s	1555m	1654s	1555s
	1514m	1540m	1540w	1560s	1530w
δ(C–H)	1396w	1395w	1396w	1395w	1395w
	1368s	1370s	1268s	1369s	1368s
	1345s	1355s	1300s	1305s	1300s
ν(C–O)	1180s	1240s	1105m		1140m
	1090s				
ν(Si–O)	1075s	1055s	1035m		1035m
ν(Si–F)	930s	930s	927s	950s	950s
	826s	878s	880s	860s	835s

[a] IA(IB) sample contained IA/IB in 19 : 1 ratio.
IIA′(IIB′) sample contained IIA′/IIB′ in 11 : 1 ratio.
IIIC(IIID) sample contained IIIC/IIID in 1 : 1 ratio.

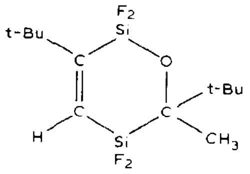
TABLE 2

MASS SPECTRAL DATA FOR IA(IB), IIA′(IIB′), IIIA, IIIC(IIID) AND IVA [a]

Ion	m/e	Abundance				
		IA(IB)	IIA′(IIB′)	IIIA	IIIC(IIID)	IVA
C_2HO^+	41					73
$C_2H_3O^+$	43		6	16		
$C_4H_9{}^+$	57	8	100	100	100	87
$C_5H_7{}^+$	67			1	19	
$C_5H_9{}^+$	69		25			
$C_4H_6O^+$	70					100
$C_6H_5{}^+$	77	5				
$C_6H_{10}{}^+$	82			10	35	67
$C_5H_8O^+$	84		97			
$C_6H_{12}O^+$	100		7			
$C_7H_5O^+$	105	100				
$C_5H_7SiF_2{}^+$	133		1	6	44	21
$C_6H_{10}SiF_2{}^+$	148		2	7	73	7
$C_7H_{13}SiF_2{}^+$	163			3		
$C_{13}H_{10}$	166	79				
$C_6H_{10}SiF_3{}^+$	167				4	5
$C_{13}H_{10}O^+$	182	97				
$C_6H_{10}Si_2F_4{}^+$	214	7				
$C_6H_{11}Si_2F_4{}^+$	215		2	15		25
$C_5H_8Si_2F_5{}^+$	219				5	
$C_6H_{10}Si_2F_4O^+$	230	3		9		
$C_6H_{11}Si_2F_5{}^+$	234				9	
$C_8H_{11}Si_2F_4O^+$	255			23		
$C_8H_{13}Si_2F_4O^+$	257		14			
$C_9H_{13}Si_2F_4O^+$	269					3
$C_9H_{14}Si_2F_4O^+$	270			77		
$C_{10}H_{16}Si_2F_4O^+$	284					5
$C_{11}H_{19}Si_2F_4O^+$	299		3			
$C_{12}H_{22}Si_2F_4O^+$	314		1			
$C_{15}H_{11}Si_2F_4O^+$	339	1				
$C_{18}H_{17}Si_2F_4O^+$	381	3				
$C_{19}H_{20}Si_2F_4O^+$	396	6				

[a] Same samples as in Table 1.

There are three products in the reaction with pinacolone. In addition to a small amount of the ring product IIA, two isomers of the product from hydrogen abstraction, IIA′ and IIB′ were obtained.



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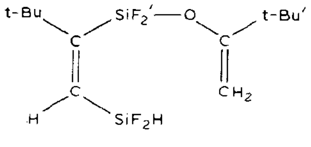
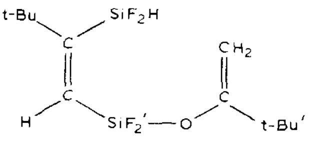


(II A′)



(II B′)

TABLE 3. NMR DATA FOR COMPOUNDS IA, IB, IIA, IIIA AND IVA [a]

Compound	t-Bu	H(C)	H(A),H(B)	R	R′	F(A),F(B)	F(A′),F(B′)	Coupling constant (Hz)
IA	1.19(s)	6.40(m)		Ph, 7.23(c)	Ph, 7.23(c)	138.6(A_2,d)	136.5(A_2,d)	J(H–F(A)) = J(H–F(B)) = 4 J(H–F(A′)) = J(H–F(B′)) = 3.5
IB						137.3(A_2,d)	135.1(A_2,d)	J(H–F(A)) = J(H–F(B)) = 3 J(H–F(A′)) = J(H–F(B′)) = 2.8
IIA	1.17(s)	6.50(m)		CH_3, 1.80(s)	t-Bu, 1.10(s)	142.9(AX,u)	128.3(AX,u)	
IIIA	1.20(s)	6.39(m)	6.15 4.90 $(AB,_{t})$	H, 1.80(s)	H, 1.80(s)	130.2(A_2,u)	136.8(A_2,u)	J(H(C)–F(A)) = J(H(C)–F(B)) = 4.7 J(F–F′) = 1 J(H(A)–H(B)) = 5.7 J(H(B)–R) = 6.5
IVA	1.18(s)	6.31(t)	6.19 4.80 $(AB,_{d})$	H, 2.08(m)	CH_3, 1.42(br)	133.2 139.8 $(AX,^{d}_{d,d})$	134.8 141.3 $(AX,_{d})$	J(H(C)–F(A)) = 3 J(R–R′) = 8, J(R–F(B)) ≈ 0 J((R–F(A) = 8.5, J(H(A)–H(B)) = 5.7 J(H(B)–R) = 6, J(F(A)–F(B)) = 20 J(F(A′)–F(B′)) = 56, J(F–F′) = 3

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

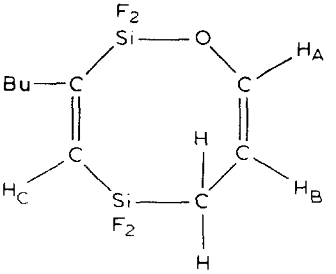
TABLE 4. NMR DATA FOR COMPOUNDS II(A′), II(B′), III(C) AND III(D) [a]

Compound	t-Bu	H	CH_2	R′	Si–H	F	F′	Coupling constant (Hz)
II(A′)	1.17(s)	6.50(m)	4.30(br)	t-Bu 1.10(s)	5.10(t,t)	136.1(d,m)	132.7(m)	J(H–F) = 6.8, J(H–F′) = 3.4 ^2J(SiH–F) = 68, J(F–F′) = 5
II(B′)						137.5(d,m)	135.6(m)	^2J(SiH–F) = 68, J(F–F′) = 5 J(H–F′) = 5.5
III(C)	1.20(s)	6.40(m)			5.10(t,t)	140.6(d,m)	133.2(m)	J(H–F′) = 3.9 ^2J(SiH–F) = 68 J(F–F′) = 6
III(D)	1.20(s)	6.40(m)			5.10(t,t)	137.5(d,m)	135.5(m)	J(H–F′) = 5.6 ^2J(SiH–F) = 68 J(F–F′) = 5

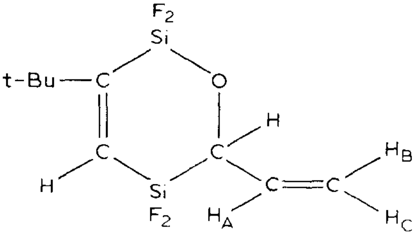
[a] Proton chemical shift δ in ppm, ^{19}F chemical shift in ppm upfield from internal reference CCl_3F.

The characteristic spectral features of the -SiF_2H group are shown in both ^1H and ^{19}F NMR spectra. The ^1H NMR spectra show a large triplet ($^2J(HF) = 68$ Hz) of triplets at δ 5.1 ppm. The ^{19}F NMR spectra also show a large doublet ($^2J(HF) = 68$ Hz) of multiplets which reduces to one multiplet on proton-noise decoupling. The ^1H NMR spectra also show two singlet peaks at δ 1.17 and 1.10 ppm for t-Bu and t-Bu′, respectively, a multiplet at δ 6.5 ppm for the vinyl proton, and a broad peak at δ 4.3 ppm characteristic of $-O-\overset{|}{C}=CH_2$. The peak intensity ratio also agrees with the proposed structure. The differentiation of these two isomers is achieved by comparing the HF coupling constants in the multiplets for -$OSiF_2$ groups in the two isomers in the $^{19}F\{^{19}F\}$ NMR spectrum. The multiplet at 132.7 ppm shows smaller H–F coupling than does the one at 135.6 ppm under irradiations at 136.1 and 137.47 ppm, respectively (Table 4).

Only one product, compound IIIA, was obtained in the fraction collected at -15°C in the reaction with acrolein. The mass spectral data (Table 2) show clearly that the compound has a molecular formula of $C_9H_{14}Si_2F_4O$. The IR data (Table 1) show the absence of ν(C=O) and the presence of C–O and Si–O bands. No ν(Si–H) was observed. These results suggest that $C_9H_{14}Si_2F_4O$ has a ring structure. In this case, two possible structures, IIIA and XA, should be considered, although the IR data favor the structure of IIIA (lack of characteristic bands of vinyl group).



(III A)



(X A)

The ^1H NMR spectrum of IIIA (Fig. 1a) shows a singlet at δ 1.2 ppm for the t-butyl group. In the region of δ 4–6.5 ppm no ABC spectrum typical of vinyl protons is observed. Instead, the triplet at δ 6.39 ppm may be assigned to H(C) of structure IIIA, the doublet at δ 6.15 ppm and the quartet at δ 4.90 ppm form an AB system with the B half being further split into overlapping triplets. These signals are of H(A) and H(B) of IIIA. The complex peak at δ 1.80 ppm may be assigned to the CH_2 group of IIIA. The intensity ratio of these resonances agrees with the structure of IIIA. When the peak at δ 1.80 ppm (assigned to CH_2) is irradiated the "quartet" at δ 4.90 ppm reduces to a doublet.

The ^{19}F NMR spectrum of IIIA shows two broad singlets at 130.2 and 136.8 ppm. In the ^1H-decoupled spectrum, both reduce to a triplet. When the peak at 136.8 ppm is irradiated, the peak at 130.2 ppm shows complex resonances due to H–F couplings that only an A-type ring structure would show. The off-resonance ^{13}C NMR spectrum (Fig. 1b) shows a quartet at δ 29.3 ppm and a singlet at δ 40.5 ppm, which are due to the carbons in the tert-butyl group. Four resonances appear in the region of sp^2 carbons, among which the two doublets at δ 105.8 and 138.0 ppm are the signals from C(6) and C(7); the other two complex resonances (due to F

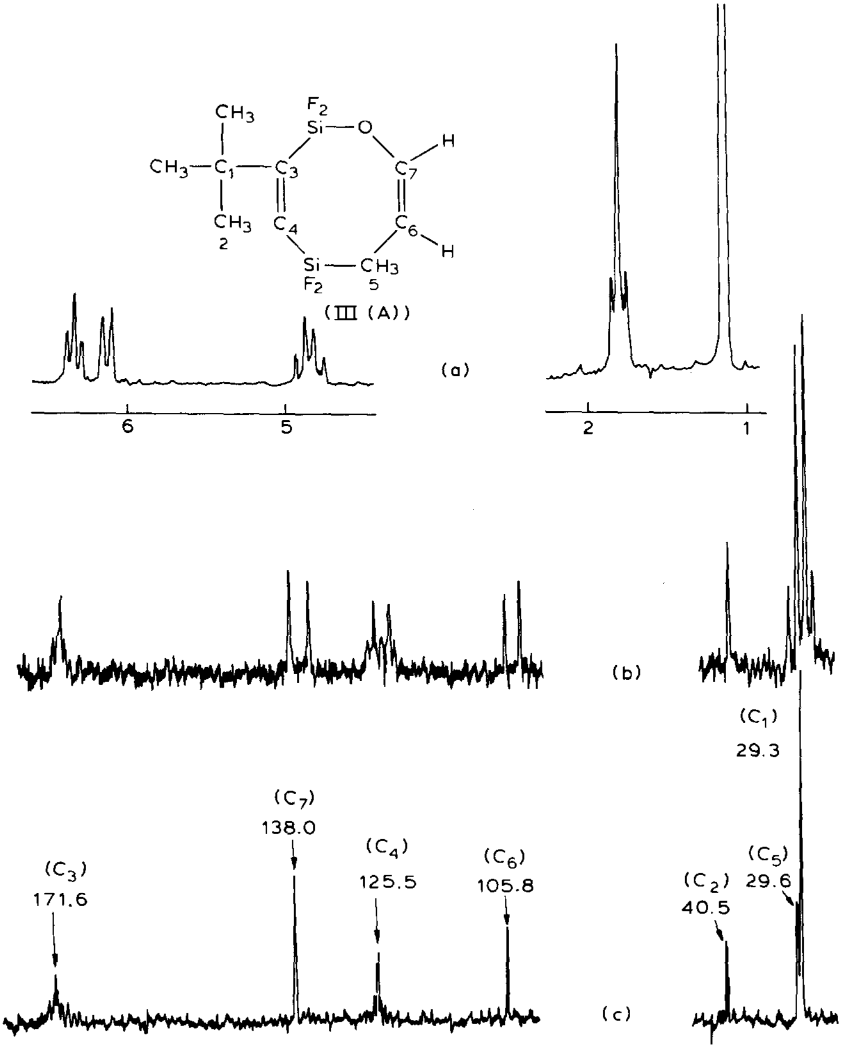


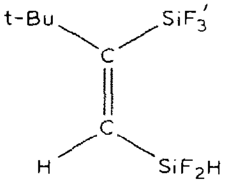
Fig. 1. (a) ^{1}H NMR spectrum of compound IIIA. (b) Off-resonance ^{13}C NMR spectrum of compound IIIA. (c) Proton-noise decoupled ^{13}C NMR spectrum of compound IIIA.

couplings) at δ 125.5 and 171.6 ppm belong to C(4) and C(3), respectively, the latter being shifted down field by the adjacent tert-butyl group and the SiF_2 group. Using the empirical formula we developed to account for this type of compound [7], the chemical shift of C(3) can be calculated to be δ 174 ppm, in reasonably good agreement with the observed value. The peak for C(5) at δ 29.6 ppm is buried in the quartet of C(1), but can be observed clearly in the proton-noise decoupled spectrum (Fig. 1c).

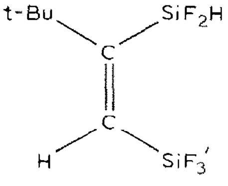
The fraction collected at −45°C from the reaction with acrolein contains two isomers of molecular formula $C_6H_{11}Si_2F_5$ (Table 2). The IR spectrum of this fraction shows a sharp absorption at 2244 cm^{-1} which is typical of ν(Si–H) in the

SiF_2H group. The ^1H NMR spectrum also shows, in addition to the singlet for the tert-butyl protons (δ 1.2 ppm) and the multiplet for the vinyl proton (δ 6.4 ppm), a large triplet ($J = 68$ Hz) of quartets at δ 5.1 ppm. The ^{19}F NMR spectrum shows two sets of spectra, each consisting of a multiplet and a large doublet ($J = 68$ Hz) of multiplets. In the ^1H-decoupled spectrum, the large doublets of multiplets reduce to single multiplet. In each set, the intensity ratio of the two resonances is 3 : 2.

All the spectral evidence clearly suggests that the two isomers of formula $C_6H_{11}Si_2F_5$ resulted from hydrogen and fluorine abstraction, with no $CH_2{=}CH{-}CHO$ being incorporated. The structures that fit all these spectral data are IIIC and IIID.



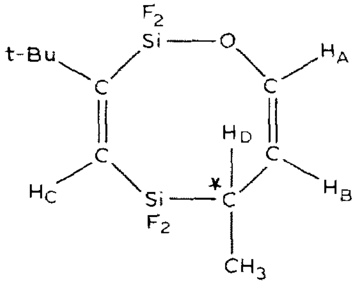
(III C)



(III D)

The $^{19}F\{^{19}F\}$ NMR spectrum shows that the peaks at 135.5 and 137.5 ppm are due to the SiF_3 and SiF_2H groups of one isomer and the peaks at 133.2 and 140.6 ppm are due to the SiF_3 and SiF_2H groups of the other. The coupling constant between the vinyl proton and the fluorines in SiF_3 is 3.9 Hz for the peak at 133.2 ppm and 5.6 Hz for the peak at 135.5 ppm. Based on these values, we assign the peaks at 133.2 and 140.6 ppm to IIIC and peaks at 135.5 and 137.5 ppm to IIID. The reasons for the formation of these compounds are not clear.

There is only one product from the reaction with crotonaldehyde. The mass spectrum shows the parent ion of $C_{10}H_{16}Si_2F_4O$. The IR spectrum is very similar to that of IIIA. The structure that fits all the spectral data is IVA.



(IV A)

All the NMR parameters are shown in Table 3. As in the case of IIIA, the triplet at δ 4.80 ppm and the doublet at δ 6.19 ppm in the ^1H NMR spectrum are actually an AB system with the high-field half being split further into overlapping doublets. On irradiating at the methine proton signal at δ 2.08 ppm, the "triplet" reduces to a doublet. The ^{19}F NMR spectrum shows two sets of AX spectra with equal intensity. It is clear that the AX spectra are caused by the asymmetric *C center in the ring.

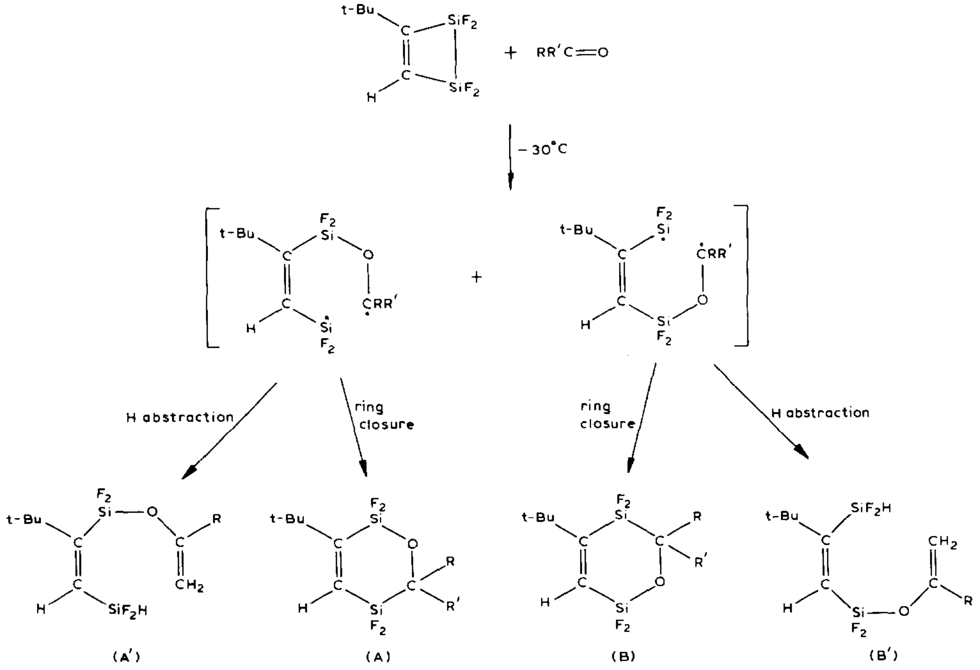
It is known that in these ring compounds the AX spectrum with the larger J(AX)

(50–60 Hz) is due to the -OSiF_2- group and that the other AX with smaller J(AX) (~ 20 Hz) is due to the SiF_2 group bonded to the asymmetric carbon [1]. In this case the AX spectrum with larger F–H couplings at 133.1, 133.3, 139.7 and 139.9 ppm belongs to the $F_2Si-C^\star$ group. Only an A-type ring structure would have the complicated H–F coupling pattern at 139.7 and 139.9 ppm. No evidence for the B-type isomer of $C_{10}H_{16}Si_2F_4O$ was observed.

As was found in the reactions with acetaldehyde, propionaldehyde, benzaldehyde and acetone, the reactions studied in the present work seem to involve a diradical intermediate. Schemes 1 and 2 illustrate the reactions mechanisms.

Three interesting comparisons may be considered: (i) A-type product vs. B-type, (ii) ring closure vs. H abstraction, and (iii) six-membered ring vs. eight-membered ring. In all cases A-type products were produced overwhelmingly. It is believed that the silicon of the SiF_2 group closer to the tert-butyl group has greater affinity for the carbonyl oxygen [1]. The electron-releasing ability of R and R′ and the steric interaction between R and R′ groups and the tert-butyl group may also enhance the selectivity [1]. The combined influence of inductive and steric effects on the relative yields of the products can be seen from Table 5. In the cases of aldehydes (R = H, R′ = alkyl) the steric effect keeps the R′ alkyl groups away from the -SiF_2- radical of the intermediate, so that ring closure proceeds more easily. In the case of acetone

Scheme 1

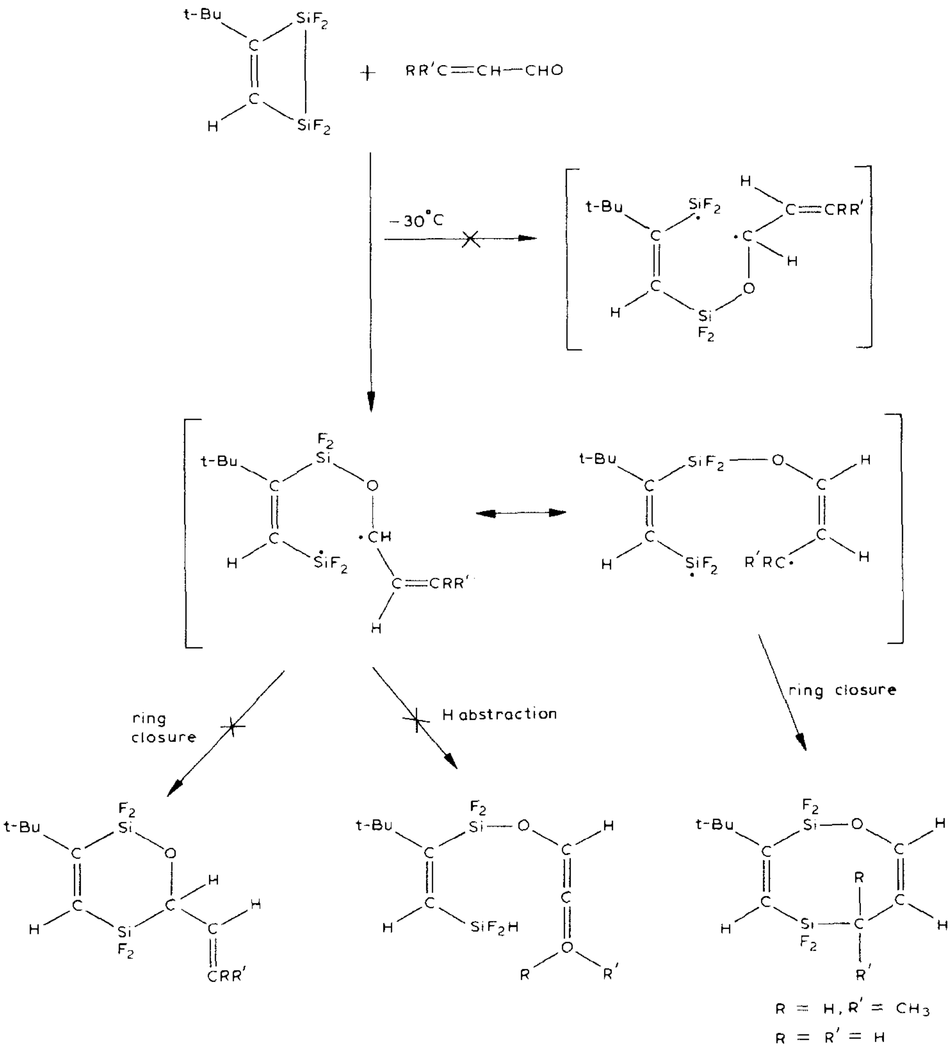


R = CH_3, R′ = t-Bu
R = R′ = CH_3

R = H, R′ = CH_3, C_2H_5, C_6H_5
R = R′ = C_6H_5
R = CH_3, R′ = t-Bu
R = R′ = CH_3, only A was obtained

R = CH_3, R′ = t-Bu
R = R′ = CH_3

Scheme 2

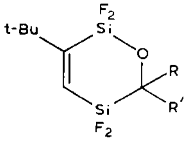


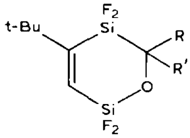
$(R = R' = CH_3)$, hydrogen abstraction by the -SiF_2- group from CH_3 becomes unavoidable no matter what orientation the intermediate may take. In the reaction of pinacolone (R = t-Bu, $R' = CH_3$), one may expect that the bulky t-Bu group would hinder ring closure so that hydrogen abstraction from CH_3 would become more pronounced. This is what was observed. In the case of conjugated aldehydes, the resonance effect predominates. The resonance structure of the diradical intermediate would favor the formation of the eight-membered ring over the six-membered ring. The contribution of the resonance structures of $RR'C{=}C{-}CH{=}O \leftrightarrow RR'\overset{+}{C}{-}C{=}CH{-}\bar{O}$ would increase the negative charge on the oxygen, so that the selection of A-type is greatly favored. In fact, in both reactions with acrolein and crotonaldehyde, A-type eight-membered rings are the only products obtained.

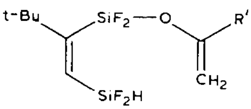
TABLE 5

RELATIVE YIELDS OF THE REACTION PRODUCTS

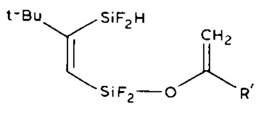
Reactant, RR'C=O		Relative yield (%)			
R	R'	A	B	A'	B'
H[a]	CH_3	76	24		
H[a]	C_2H_5	93	7		
H[a]	C_6H_5	92	8		
H	$CH_2=CH$-	100			
H	$CH_3CH=CH$-	100			
C_6H_5	C_6H_5	95	5		
CH_3[a]	CH_3	11		74	15
CH_3	t-C_4H_9	4		88	8



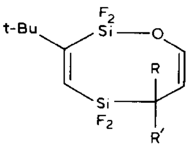




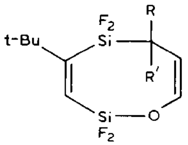
(A')



(B')



(A)



(B)

[a] ref. 1

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