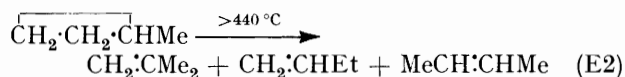


Cyclopropane Chemistry. Part 4.¹ The Reactions of 1,2,2-Trifluoroethylidene with Alkenes and Pyrolysis of the Resulting Cyclopropanes²

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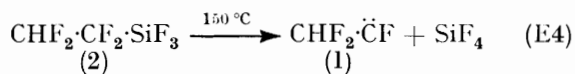
1,2,2-Trifluoroethylidene, generated by the pyrolysis of (1,1,2,2-tetrafluoroethyl)trifluorosilane, reacts with tetrafluoroethylene, ethylene, and a series of methyl-substituted ethylenes to give the corresponding 1-fluoro-1-difluoromethylcyclopropanes in good yield; cyclohexene gives the corresponding norcarane, and tris(trifluoromethyl)phosphine gives the corresponding phosphorane $(CF_3)_3P^+ \cdot CF^- \cdot CHF_2$. Pyrolysis of 1,2,2,3,3-pentafluoro-1-difluoromethylcyclopropane affords difluorocarbene and 3*H*-pentafluoropropene, but pyrolysis of the methyl-substituted cyclopropanes results in the formation of dienes in high yield, e.g. the 1,4-dienes $CHF:CF \cdot CMeR \cdot CMe:CH_2$ from the cyclopropanes $\overline{CMe_2 \cdot CMeR \cdot CF \cdot CHF_2}$ ($R = H$ or Me) or 1,3-dienes from the methyl-substituted cyclopropanes, e.g. $\overline{CMe_2 \cdot CH_2 \cdot CF \cdot CHF_2} \rightarrow CH_2:CMe:C(CHF_2):CH_2$. In certain cases further dehydrofluorination of the 1,3-dienes affords trienes, e.g. $\overline{CMe_2 \cdot CMe_2 \cdot CF \cdot CHF_2} \rightarrow CH_2:CMe:C(:CHF) \cdot CMe:CH_2$.

PYROLYSIS of fluorocyclopropane,³ methylcyclopropane,⁴ and 1,1-dimethylcyclopropane⁵ gives isomeric olefins as follows:



Although some 1,1-difluorocyclopropanes eliminate difluorocarbene when heated,^{1,6} others, e.g. 1,1,2-trifluoro-2-trifluoromethylcyclopropane,¹ rearrange to alkenes.

1,2,2-Trifluoroethylidene (1), readily formed by the gas-phase pyrolysis of (1,1,2,2-tetrafluoroethyl)trifluorosilane (2),^{7,8} rearranges in the absence of a substrate to trifluoroethylene, which is then attacked by the carbene to give *cis*- and *trans*-1,2,2,3-tetrafluoro-1-difluoromethylcyclopropane (3).⁸



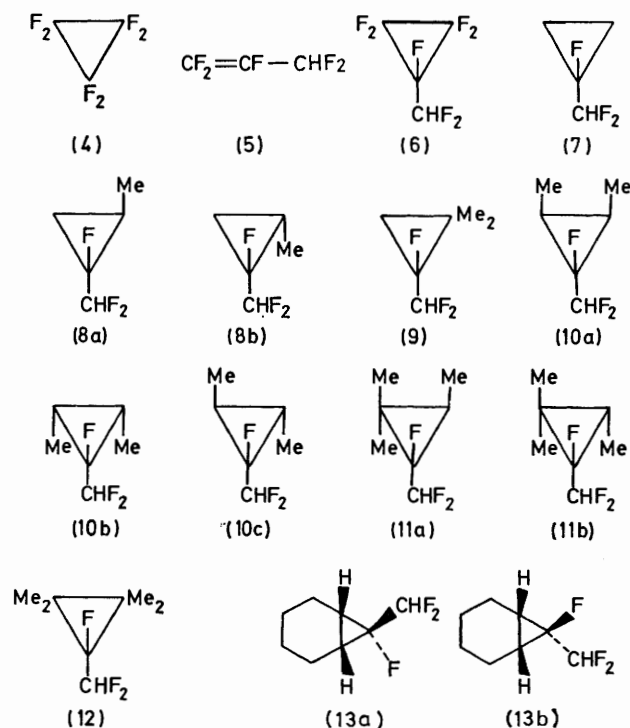
The additions of carbene (1) to ethylene, a series of methyl-substituted ethylenes, tetrafluoroethylene, cyclohexene, and tris(trifluoromethyl)phosphine have now been carried out, and the pyrolyses of a number of the resulting cyclopropanes have been investigated.

RESULTS AND DISCUSSION

Reactions of the Carbene (1).—Gas-phase pyrolysis of mixtures of the carbene precursor (2) and an excess of the individual alkenes at 150 °C (maximum pressure *ca.* 1 atm) for 15–18 h gave the results shown in Table 1.

The ¹⁹F n.m.r. spectra of the cyclopropanes (7)–(12) have been discussed in detail previously and stereochemical assignments made,⁹ and the structures of the

norcaranes (13a) and (13b) were assigned on the basis of (i) the chemical shifts of the tertiary fluorine atoms [(13a) *endo* (F *trans* to H) 149.5 p.p.m. (relative to CF_3CO_2H); (13b) *exo* (F *cis* to H) 120.0 p.p.m., *cf.* (10a) 154.3 p.p.m. and (10b) 119.8 p.p.m.] and (ii) their



g.l.c. retention times [(13b) > (13a), *cf.* (10b) > (10a)]. The ¹H and ¹⁹F n.m.r. spectra of cyclopropane (6) were in complete agreement with the proposed structure.

The stereospecific additions to *cis*- and *trans*-but-2-ene are consistent with carbene (1) being generated in the singlet state, which is in agreement with the observation that insertion of the carbene into the tertiary C–H bond of the ether $L-Me[CH_2]_5CH(Me)OMe$ occurs with complete retention of configuration.¹⁰

One noteworthy feature of the reactions with the

TABLE 1
 Reactions of carbene (1) with alkenes

Alkene	Ratio (2) : alkene	Cyclopropanes (%)	Other products (%)				
			SiF ₄	CHF ₂ CF ₂	(3)	(4)	(5)
CF ₂ :CF ₂	1 : 10	(6) 74	100	10		Trace	5
CF ₂ :CF ₂	1 : 10 *	(6) 71	98	8		Trace	19
CH ₂ :CH ₂	1 : 10	(7) 82	99	5			
CH ₂ :CHMe	1 : 15	(8a) 55 (8b) 33	97	9	2		
CH ₂ :CMe ₂	1 : 10	(9) 88	93	9	1		
<i>cis</i> -MeCH:CHMe	1 : 7	(10a) 55 (10b) 27	96	15	1		
<i>trans</i> -MeCH:CHMe	1 : 15	(10c) 85	98	11	1		
MeCH:CMe ₂	1 : 7	(11a) 47 (11b) 34	96	16	Trace		
Me ₂ C:CMe ₂	1 : 10	(12) 86	99	6			
CH:CH·[CH ₂] ₃ ·CH ₂	1 : 9.5	(13a) 45 (13b) 17	98	33	4		

* Carried out at 200 °C (10 h).

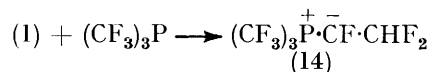
methyl-substituted ethylenes was that carbene (1) insertion into the allylic C-H bonds of the olefins was not detected. Carbene (1) has been observed previously to insert into primary, secondary, and tertiary C-H bonds of alkanes^{2,11,12} and alkyltrimethylsilanes.¹³

The addition of carbene (1) to cyclohexene was much less favourable than addition to the other alkenes as shown by the relatively low yield (62%) of norcarane (13) and the increased yield of trifluoroethylene plus cyclopropane (3). From the reactions with propene, *cis*-but-2-ene, and 2-methylbut-2-ene it is apparent that carbene (1) adds predominantly in the direction in which there is least steric hindrance between the methyl groups in the olefin and the CHF₂ group in the attacking carbene, *i.e.* the cyclopropanes (8a), (10a), and (11a) are formed, respectively, as the major isomers with these alkenes. Similarly, with cyclohexene the major norcarane isomer (13a) formed is that in which the CHF₂ group and the cyclohexane ring are *trans*.

In the reactions of carbene (1) with tetrafluoroethylene, compounds (4) and (5) are formed as minor products *via* decomposition of cyclopropane (6); this decomposition is discussed later.

The reaction of the carbene precursor (2) with tris(trifluoromethyl)phosphine (1 : 10 molar ratio) at 150 °C (5 h) gave unchanged phosphine (91% recovered), silicon tetrafluoride (95%), trifluoroethylene (15%), 1,2,2-trifluoroethylidene tris(trifluoromethyl)phosphorane (14) (37%), a higher-boiling unidentified yellow oil (12% by weight), and tar.

Pyrolysis of the Cyclopropanes.—The pyrolysis of cyclopropane (6) was investigated under various conditions, *i.e.* static alone, in the presence of glass wool, and in the presence of an excess of cyclohexene; and *flow*



at low pressure (1–2 mmHg) alone and in the presence of an excess of cyclohexene: the results obtained are shown in Table 2.

The products obtained show conclusively that cyclopropane (6) decomposes thermally to give olefin (5) and difluorocarbene; the carbene can be trapped by cyclohexene to afford the norcarane (15) [equation (E6)], but in the absence of a trap the reactions shown in equations (E7)–(E9) take place.

Under static conditions considerable reaction of the carbene with the walls of the reaction tube takes place to give carbon monoxide and silicon tetrafluoride, and in the presence of glass wool such reaction is virtually quantitative. However, pyrolysis under flow conditions at low pressure favours dimerisation of the carbene and further reaction of the tetrafluoroethylene so formed. In the flow pyrolysis a small amount (3%) of hexafluoropropene was isolated which probably arises by rearrangement of cyclopropane (4); pyrolysis of octafluorocyclobutane at *ca.* 550 °C¹⁴ and cyclopropane (4) at *ca.* 450 °C¹⁵ affords hexafluoropropene.

 TABLE 2
 Pyrolysis of cyclopropane (6)

Type	Added material	Temperature (°C)	Time/h	Recovered (6) (%)	Products (%)					
					(4)	(5)	C ₂ F ₄	<i>cyclo</i> -C ₄ F ₈	CO	SiF ₄
Static		150	16	93	<i>a</i>	98	Trace	<i>a</i>	<i>a</i>	
Static		200	320	0	16	99	30	6	46	47
Static		300	160	0	6	100	28	12	50	49
Static	Glass wool	200	320	0		100	Trace		99	99
Static	Cyclohexene	200	320	0		99	14	Trace	11	13
Flow		375	2.3 s ^b	0		98	58	33	Trace	Trace
Flow	Cyclohexene	375	2.4 s ^b	0		98	36	22		39

^a Not recorded. ^b Contact time. ^c Hexafluoropropene (3%) also formed.

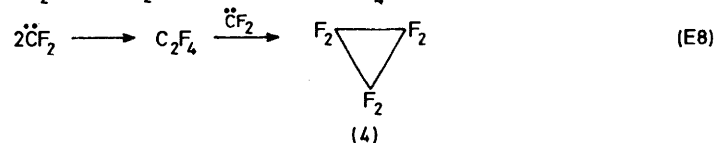
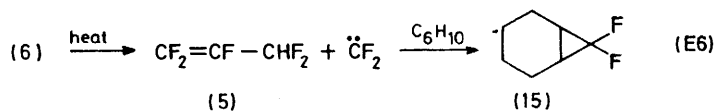
TABLE 3
Pyrolysis of methyl-substituted cyclopropanes

Cyclopropane (8a) + (8b)	Temperature (°C)	Cyclopropane recovered (%)	Products (%)				
			1,3-Diene		1,4-Diene		Triene
(8a) + (8b)	750	(8a) 2 (8b) 63	(18) 85	(24) ca. 4			Five, ca. 2
(8a) + (8b)	710	(8a) 49 (8b) 80	(18) 71	(24) ca. 3.5			Five, ca. 4.5
(9)	685	62	(19) 18				Three, trace; Polymer, 41
(9)	700	2	(19) 97				Three, trace
(9)	700 *	5	(19) 84				Three, trace; Polymer, 12
(10a) + (10b)	700	(10a) 18 (10b) 55	(20) 81	(25) ca. 5	(26) 6		One, ca. 4
(10c)	705	(10c) 2 (10a) ca. 0.5 (10b) ca. 0.5	(20) 95	(25) ca. 1	(26) ca. 3		Two, trace
(10c)	690 *	(10c) 35 (10a) ca. 1.5 (10b) ca. 1	(20) 45	(25) ca. 2	(26) ca. 2		Two, trace Polymer, 10
(11a) + (11b)	720		(21a) 40 (21b) 7 (22) 10		(27) 37		Tar, 14 Seven, 3
(11a) + (11b)	270	(11a) 22 (11b) 33	(21b) ca. 1.5	(16a) 57 (16b) 23	(27) 2		Two, ca. 1
(12)	720		(23) 38		(28) 47		Eight, 8
(12)	680	4	(23) 65	(17) ca. 1.5	(28) 27		Three, 4
(12)	270		(23) 1	(17a) 55 (17b) 37			Tar

* Products not treated with KOH.

The amount of thermal decomposition of cyclopropane (6) was approximately half that found in the preparation of cyclopropane (6) from carbene (1) and tetrafluoroethylene under identical conditions of temperature and time, *i.e.* 150 °C (16 h) 7 and 13%, 170 °C (8 h) 8 and

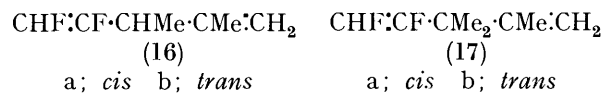
was recovered unchanged after heating at 250 °C (70 h) and the cyclopropane isomers (10) were stable at 300 °C (8—18 h). A further introduction of methyl groups into the cyclopropane ring, however, resulted in considerable thermal instability. Thus a mixture of the cyclo-



16%, and 200 °C (5 h) 11 and 21%, respectively, suggesting that the cyclopropane (6) is formed in a vibrationally excited state¹⁶ which, unless the excess energy is rapidly removed by collision, results in decomposition to alkene (5) and difluorocarbene.

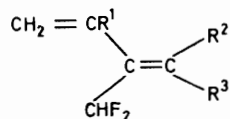
1-Fluoro-1-difluoromethylcyclopropane (7) was considerably more thermally stable than cyclopropane (6) and was recovered unchanged (91%) when heated at 380 °C (20 h); no evidence was obtained for the elimination of carbene (1). A preliminary investigation showed that the 1-fluoro-1-difluoromethylmethylcyclopropanes (8a and 8b) were thermally stable when heated in the range 250—300 °C for several hours; cyclopropane (9)

propanes (11a) and (11b) at 270 °C (20 h) gave unchanged (11a) (33% recovered), unchanged (11b) (22% recovered), *cis*- and *trans*-1,2-difluoro-3,4-dimethylpenta-1,4-diene (16) (80%), silicon tetrafluoride (87%), other minor products, and tar. Under identical conditions the tetramethyl analogue (12) decomposed completely to



give mainly silicon tetrafluoride (83%) and *cis*- and *trans*-1,2-difluoro-3,3,4-trimethylpenta-1,4-diene (17) (92%).

The flow pyrolyses of the cyclopropanes (8)–(12) at low pressure (*ca.* 3 mmHg) in the temperature range 680–750 °C (contact time <0.5 s) gave products which readily polymerised unless they were treated with solid potassium hydroxide to remove silicon tetrafluoride and other acidic impurities. The results obtained from these pyrolyses and from the lower-temperature pyrolyses of cyclopropanes (11) and (12) are shown in Table 3.



- (18) $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$
 (19) $\text{R}^1 = \text{Me}, \text{R}^2 = \text{R}^3 = \text{H}$
 (20) $\text{R}^1 = \text{R}^2 = \text{H}, \text{R}^3 = \text{Me}$
 (21) a; $\text{R}^1 = \text{R}^3 = \text{Me}, \text{R}^2 = \text{H}$
 b; $\text{R}^1 = \text{R}^2 = \text{Me}, \text{R}^3 = \text{H}$
 (22) $\text{R}^1 = \text{H}, \text{R}^2 = \text{R}^3 = \text{Me}$
 (23) $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Me}$

cis/trans - CHF:CF·CHR·CH:CH₂

(24) $\text{R} = \text{H}$ (25) $\text{R} = \text{Me}$

$\text{CH}_2:\text{CR}^1\cdot\text{C}(\text{CHF})\cdot\text{CR}^2:\text{CH}_2$

(26) $\text{R}^1 = \text{R}^2 = \text{H}$

(27) $\text{R}^1 = \text{H}, \text{R}^2 = \text{Me}$

(28) $\text{R}^1 = \text{R}^2 = \text{Me}$

It was not found possible to obtain correct carbon analyses for the 1,3-dienes and trienes, presumably because of partial decomposition and polymerisation, but the n.m.r. and mass spectral data obtained were entirely consistent with the proposed structures.

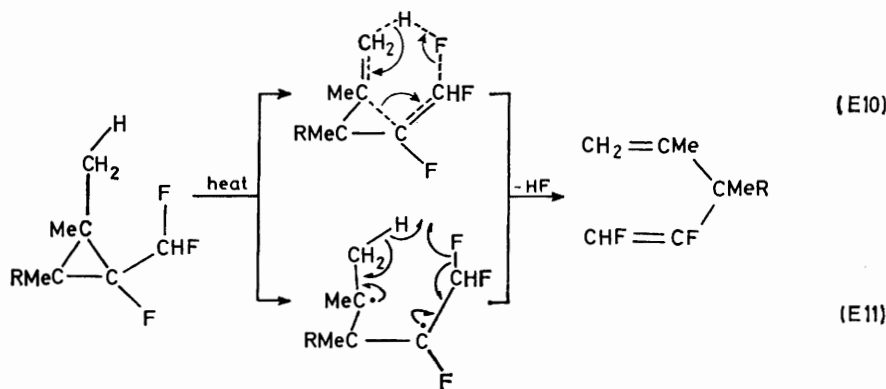
The lower-temperature static pyrolyses (270 °C) of

not favourably orientated. It is therefore, considered that elimination probably involves formation of the more stable diradical ($-\dot{\text{C}}\text{Me}_2 > -\dot{\text{C}}\text{HMe}$).

In the higher-temperature flow pyrolyses (*ca.* 700 °C) elimination of the tertiary fluorine and a methyl hydrogen leading to 1,3-dienes was the favoured reaction. It was considered possible that in these reactions 1,4-dienes were initially formed, which then rearranged to 1,3-dienes. However, when a mixture of the 1,4-dienes (17a and b) was flow-pyrolysed at 720 °C a complex mixture of products was obtained, which contained only trace amounts of the 1,3-diene (23) and the triene (28). Also pyrolysis of the 1,4-dienes in the presence of silicon tetrafluoride did not result in any appreciable rearrangement. It is therefore probable that the 1,3-dienes are formed by an elimination process in which 1,4-dienes are not intermediates.

Possible mechanisms leading to the 1,3-dienes are (a) concerted elimination and ring opening [equation (E12)], (b) ring fission and elimination from the resulting diradical [equation (E13)], and (c) rearrangement *via* a fluorine shift and elimination from the resulting alkene [equation (E14)].

It is unlikely that a concerted mechanism is in operation since it would be favourable only with cyclopropanes in which the tertiary fluorine atom and the methyl group are in a *syn*-disposition. Thus although elimin-



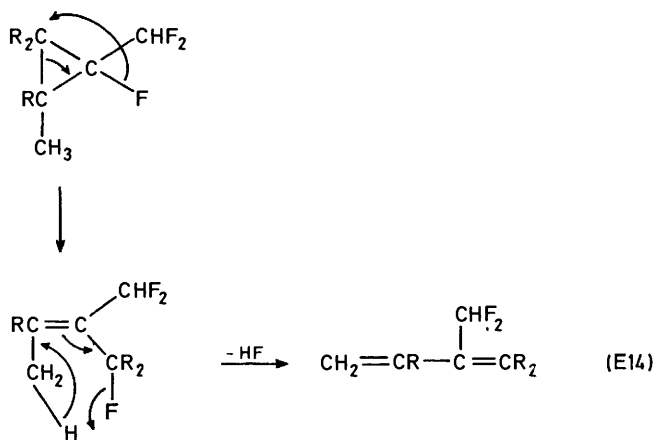
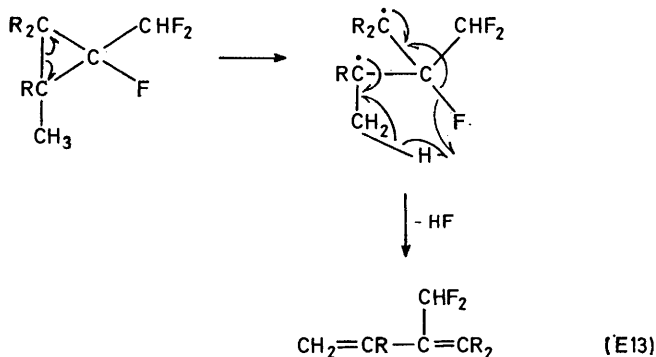
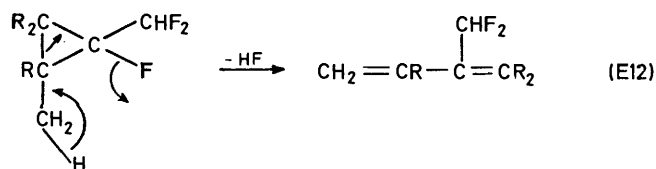
cyclopropanes (11) and (12) gave high yields of the 1,4-dienes (16) and (17), respectively. In the former reaction the 1,3-diene (21b) and the triene (27) were also obtained in low yield, while the latter pyrolysis gave a small amount of the 1,3-diene (23). The major reaction is therefore elimination of hydrogen fluoride involving a fluorine atom in the CHF_2 group and a methyl hydrogen. Such elimination could involve either a concerted elimination *via* a six-centre transition state [equation (E10)] or initial rupture of the cyclopropane ring to give an intermediate diradical [equation (E11)].

However, with the mixture of cyclopropanes (11a and b) elimination occurred only from the CMe_2 group, although in isomer (11b) the methyl in the CHMe group is favourably orientated (*cis*) for elimination to occur *via* a concerted mechanism while that in isomer (11a) is

ation from such cyclopropanes, *i.e.* (8a), (10a), and (11a), is more favoured (see Table 3) than from the corresponding *anti*-isomers, elimination from the *anti*-isomers (8b), (10b), and (11b) does occur.

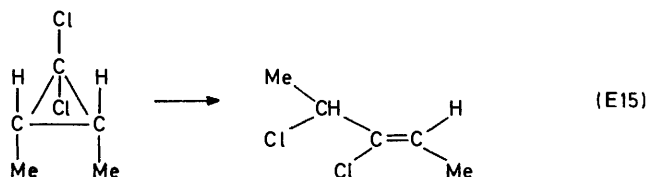
With regard to the rearrangement mechanism shown in equation (E14) it has been reported¹⁷ that thermal rearrangement of *cis*-1,1-dichloro-2,3-dimethylcyclopropane gives *trans*-3,4-dichloropent-2-ene exclusively, in which migration of the chlorine *trans* to the methyl groups occurs with simultaneous outward rotation of the methyl groups in a disrotatory manner as shown in equation (E15).

A similar rearrangement with cyclopropanes (10a) and (10b) would be expected to give the alkenes (29) and (30). Dehydrofluorination of isomer (29) would give the observed 1,3-diene (20) [equation (E16)], but de-



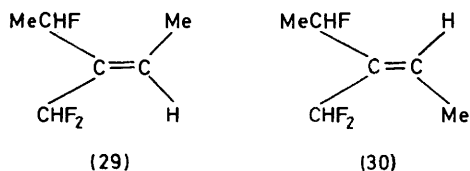
hydrofluorination of isomer (30) would be expected to afford the 1,3-diene (31) [equation (E17)] which was not detected in the products.

Although it is possible that isomerisation of alkene (30)



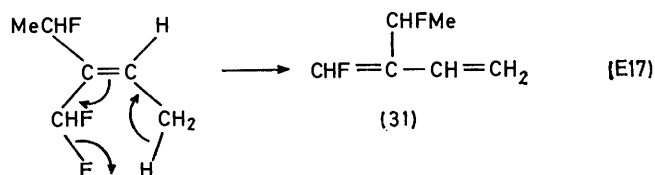
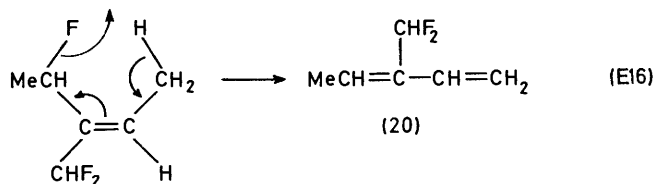
to (29) followed by elimination occurred, alkenes (29) and (30) were not detected in the products and it is unlikely that this mechanism was operative.

As expected, in the flow pyrolysis of the mixture of cyclopropanes (11a) and (11b) elimination involving the



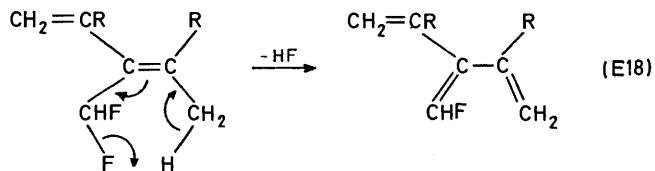
CMe_2 group is apparently more favoured than that involving the CHMe group [ratio (21) : (22) = 47 : 10], although the triene (27) (37%) also formed could arise from dehydrofluorination of diene (21a) or (22).

The results obtained are thus consistent with both 1,3- and 1,4-dienes being formed *via* diradical intermediates.



Trienes are formed by dehydrofluorination of certain of the 1,3-dienes, and are more favoured the higher the temperature; such dehydrofluorinations presumably occur *via* six-centre transition states [equation (E18)] involving the dienes (20), (21a), (22), and (23), all of which contain *syn* methyl and CHF_2 groups.

It is consistent with the proposed mechanism that trienes were not formed in the pyrolyses of the cyclopropanes (8) or (9).

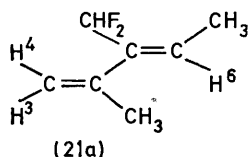
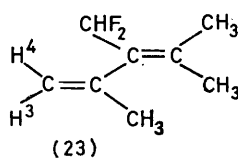
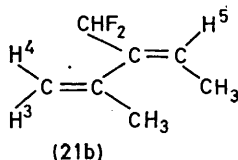
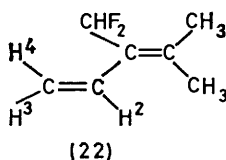
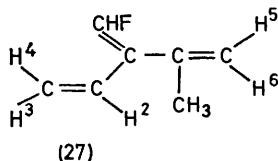
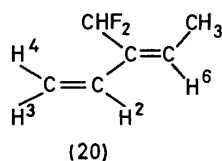
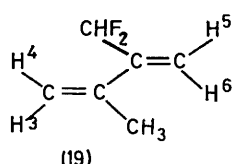
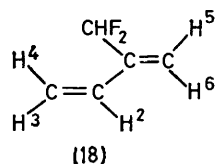


EXPERIMENTAL

Reactants and products were manipulated where possible in a conventional vacuum system to avoid contact with air or moisture. Reactions involving the carbene precursor (2) and alkenes were carried out *in vacuo* in Pyrex bulbs (*ca.* 5 dm³ for *ca.* 220 mmol of reactants and *ca.* 3.7 dm³ for *ca.* 160 mmol of reactants), fitted with a side arm, at pressures of *ca.* 1 atm, static pyrolyses in sealed Pyrex tubes (*ca.* 250 cm³) *in vacuo*, and flow pyrolyses in a silica tube (40 cm heated length, 1 cm internal diameter) at low pressure (*ca.* 3 mmHg). Products were separated by fractional condensation *in vacuo* or by g.l.c. (columns as indicated in the text) and their identities were established by molecular-weight determination, elemental analysis, i.r. spectroscopy (Perkin-Elmer spectrophotometer model 720 with sodium chloride optics), mass spectroscopy (A.E.I. MS902 instrument), and n.m.r. spectroscopy (Hitachi R20A spectrometer operating at 60 MHz for ¹H and 56.46 MHz for ¹⁹F, or a Varian HA100 instrument operating at 100 MHz for ¹H and 94.1 MHz for ¹⁹F, with reference compounds as indicated in the text). All product fractions containing silicon tetrafluoride and other components were washed with water to remove silicon tetrafluoride which was estimated by volume difference.

Carbon analyses indicated by an asterisk were low, presumably due to preliminary decomposition of the dienes.

(1,1,2,2-Tetrafluoroethyl)trifluorosilane (2) was prepared by the photochemical reaction of trichlorosilane with tetrafluoroethylene and fluorination ($\text{SbF}_3\text{-SbCl}_5$) of the resulting (1,1,2,2-tetrafluoroethyl)trichlorosilane.^{7,8} All the alkenes used were commercial samples which were carefully purified where necessary.



Hydrogen numbering system used for the dienes whose ^1H n.m.r. assignments are given in this section

Reactions of (1,1,2,2-Tetrafluoroethyl)trifluorosilane with Olefins.—(a) *With tetrafluoroethylene.* A mixture of the silane (3.72 g, 20 mmol) and tetrafluoroethylene (20.1 g, 201 mmol), heated at 150 °C (18 h), gave (i) a mixture of unchanged tetrafluoroethylene (18.1 g, 181 mmol, 90% recovered), silicon tetrafluoride (2.08 g, 20 mmol, 100%), and trifluoroethylene (0.16 g, 2.0 mmol, 10%); (ii) a mixture of hexafluorocyclopropane (4) (trace) and 3*H*-pentafluoropropene (5) (0.13 g, 1.0 mmol, 5%); and (iii) 1,2,2,3,3-pentafluoro-1-difluoromethylcyclopropane (6) (2.70 g, 14.8 mmol, 74%) (Found: C, 26.5; H, 0.6%; M^+ , 182. $\text{C}_4\text{H}_5\text{F}_7$ requires C, 26.4; H, 0.6%; M , 182), b.p. 17–18 °C; m/e 182 (10%, M^+), 181 (13, C_4F_7^+), 132 (17, $[M - \text{CF}_2]^+$), 131 (34, $[M - \text{CHF}_2]^+$), 113 (100, $[M - \text{CF}_3]^+$), 82 (46, $[M - \text{C}_2\text{F}_4]^+$), 69 (63, CF_3^+), 51 (51%, CHF_2^+), and 31 (34%, CF^+); δ_{H} 0.90 [tdt, $J_{\text{HF}}(\text{gem})$ 51.0, $J_{\text{HF}}(\text{vic})$ 13.1, and $J_{\text{HF}}(\text{trans})$ 4.1 Hz], high field from external benzene; δ_{F} 132.4 (2 F, dm, CH_2), 156.8 (4 F, A_2B_2 m, 2 CF_2 , J_{AB} 210 Hz), and 211.8 (1 F, m, CF), high field from trichlorofluoromethane.

A second reaction of the silane (3.32 g, 17.8 mmol) with tetrafluoroethylene (17.87 g, 178.7 mmol) carried out at 200 °C (10 h) gave unchanged tetrafluoroethylene (16.1 g, 161 mmol, 90% recovered), silicon tetrafluoride (1.81 g, 17.4 mmol, 98%), trifluoroethylene (0.12 g, 1.4 mmol, 8%), (4) (trace), (5) (0.45 g, 3.4 mmol, 19%), and (6) (2.31 g, 12.7 mmol, 71%).

A series of reactions was carried out under the same conditions of temperature and time as a series of decompositions of 1,2,2,3,3-pentafluoro-1-difluoromethylcyclopropane; the results are compared in the Discussion section.

(b) *With ethylene.* A mixture of the silane (3.72 g, 20 mmol) and the olefin (5.61 g, 200 mmol), heated at 150 °C (16 h), gave (i) a mixture of silicon tetrafluoride (1.87 g, 18.0 mmol, 90%) and unchanged ethylene (4.72 g, 16.8 mmol, 84% recovered); (ii) a mixture (0.33 g) of silicon tetrafluoride (0.19 g, 1.8 mmol, 9%) and material which was shown by g.l.c. (8 m Kel-F oil at 20 °C) and i.r. spectroscopy to consist of unchanged ethylene (0.05 g, 2.0 mmol, 5% recovered) and trifluoroethylene (0.09 g, 1.1 mmol, 5%); and (iii) 1-fluoro-1-difluoromethylcyclopropane (7) (1.81 g, 16.5 mmol, 82%) (Found: C, 43.9; H, 4.7%; M^+ , 110. $\text{C}_4\text{H}_5\text{F}_3$ requires C, 43.6; H, 4.5%; M , 110), b.p. 44 °C; m/e 110 (4%, M^+), 59 (100, $[M - \text{CHF}_2]^+$), and 51 (24%, CHF_2^+); δ_{H} 0.88 [1 H, td, CHF_2 , $J_{\text{HF}}(\text{gem})$ 54, $J_{\text{HF}}(\text{vic})$ 7 Hz], and 5.5–6.0 (4 H, m, C_2H_4), high field from external benzene; δ_{F} 50.2 [2 F, dd, CHF_2 , $J_{\text{FF}}(\text{vic})$ 12 Hz], and 146.0 (1 F, m, CF), high field from external trifluoroacetic acid.

(c) *With propene.* A mixture of the silane (1.86 g, 10 mmol) and the olefin (6.23 g, 148.4 mmol), heated at 150 °C (18 h), gave (i) a mixture of silicon tetrafluoride (1.01 g, 9.7 mmol, 97%) and trifluoroethylene (0.07 g, 0.9 mmol, 9%); (ii) unchanged propene (5.84 g, 139.0 mmol, 94% recovered); and (iii) a liquid mixture (1.11 g) which was separated by g.l.c. (2 m D.N.P. at 40 °C) into its components, *cis*- and *trans*-1,2,2,3-tetrafluoro-1-difluoromethylcyclopropane (3) (ca. 0.02 g, 0.1 mmol, 2%); 1-fluoro-*r*-1-difluoromethyl-*t*-2-methylcyclopropane (8a) (0.68 g, 5.5 mmol, 55%) (Found: C, 48.3; H, 5.8%; M^+ , 124. $\text{C}_5\text{H}_7\text{F}_3$ requires C, 48.4; H, 5.6%; M , 124), b.p. (Siwoloboff) 66 °C; m/e 124 (3%, M^+), 109 (5, $[M - \text{CH}_3]^+$), 73 (100, $[M - \text{CHF}_2]^+$), and 51 (37%, CHF_2^+); δ_{H} 0.86–1.36 (6 H, complex, methyl and ring protons) and 5.73 [1 H, td, CHF_2 , $J_{\text{HF}_A}(\text{gem}) = J_{\text{HF}_B}(\text{gem})$ 56, $J_{\text{HF}}(\text{vic})$ 6 Hz], low field from external tetramethylsilane; δ_{F} 50.2 [2 F, AB m, CHF_2 , $J_{\text{FF}_A}(\text{vic})$ 9, $J_{\text{FF}_B}(\text{vic})$ 9 Hz] and 141.0 (1 F, m, CF), high field from external trifluoroacetic acid; and 1-fluoro-*r*-1-difluoromethyl-*c*-2-methylcyclopropane (8b) (0.41 g, 3.3 mmol, 33%) (Found: C, 48.3; H, 5.8%; M^+ , 124), b.p. (Siwoloboff) 67 °C; m/e 124 (1%, M^+), 109 (2, $[M - \text{CH}_3]^+$), and 73 (100, $[M - \text{CHF}_2]^+$); δ_{H} 0.86–1.38 (6 H, complex, methyl and ring protons) and 5.48 [1 H, td, CHF_2 , $J_{\text{HF}_A}(\text{gem}) = J_{\text{HF}_B}(\text{gem})$ 53.7, $J_{\text{HF}}(\text{vic})$ 12.3 Hz], low field from external tetramethylsilane; δ_{F} 47.1 [1 F, ddd, CHFF_A , $J_{\text{FAFB}}(\text{gem})$ 295; $J_{\text{FF}_A}(\text{vic})$ 10 Hz], 51.8 [1 F, ddd, CHFF_B , $J_{\text{FF}_B}(\text{vic})$ 11 Hz], and 123.2 (1 F, m, CF), high field from external trifluoroacetic acid.

(d) *With 2-methylpropene.* A mixture of the silane (3.72 g, 20 mmol) and the olefin (11.2 g, 200 mmol) heated at 150 °C (15 h), gave (i) silicon tetrafluoride (1.92 g, 18.5 mmol, 93%) and trifluoroethylene (0.15 g, 1.0 mmol, 9%); (ii) unchanged 2-methylpropene (10.08 g, 180.0 mmol, 90% recovered); and (iii) 1-fluoro-1-difluoromethyl-2,2-dimethyl-

cyclopropane (9) (2.41 g, 17.5 mmol, 88%) (Found: C, 52.1; H, 6.6%; M^+ , 138. $C_6H_9F_3$ requires C, 52.2; H, 6.5%; M , 138), b.p. (Siwoloboff) 87 °C; m/e 138 (2%, M^+), 123 (14, $[M - CH_3]^+$), 103 (17, $C_5H_5F_2^+$), 87 (100, $[M - CHF_2]^+$), 51 (28%, CHF_2^+), and 42 (19%, $C_3H_6^+$); δ_H 0.78–1.04 (8 H, complex, CH_2 and 2 CH_3), and 5.55 [1 H, td, CHF_2 , $J_{HF_A}(gem) = J_{HF_B} = 54$, $J_{HF}(vic)$ 13.4 Hz], low field from external tetramethylsilane; δ_F 45.1 [1 F, ddd, CHF_A , $J_{FAFB}(gem)$ 294, $J_{FFA}(vic)$ 9 Hz], 49.6 [1 F, ddd, CHF_B , $J_{FFB}(vic)$ 11 Hz], and 133.9 (1 F, m, CF), high field from external trifluoroacetic acid; the product was shown by g.l.c. (2 m D.N.P. at 60 °C) to be contaminated with a small amount of (3) (ca. 0.02 g, 0.1 mmol, 1%).

(e) *With cis-but-2-ene*. A mixture of the silane (3.72 g, 20 mmol) and the olefin (7.84 g, 140 mmol), heated at 150 °C (18 h), gave (i) a mixture of silicon tetrafluoride (2.0 g, 19.2 mmol, 96%) and trifluoroethylene (0.25 g, 3.0 mmol, 15%); (ii) unchanged *cis-but-2-ene* (6.55 g, 117.7 mmol, 85% recovered), and (iii) a liquid mixture (2.26 g), which was separated by g.l.c. (2 m, D.N.P. at 60 °C) into its components (3) (ca. 0.02 g, 0.1 mmol, 1%); 1-fluoro-r-1-difluoromethyl-t-2,3-dimethylcyclopropane (10a) (1.50 g, 10.9 mmol, 55%) (Found: C, 52.2; H, 6.7%; M^+ , 138. $C_6H_9F_3$ requires C, 52.2; H, 6.5%; M , 138), b.p. (Siwoloboff) 86 °C; m/e 138 (0.4%, M^+), 123 (1, $[M - CH_3]^+$), 87 (12, $[M - CHF_2]^+$), 57 (100, $C_3H_2F^+$), 51 (13, CHF_2^+), and 41 (60, $C_3H_5^+$); δ_H 0.86 (6 H, m, 2 CH_3), 0.98 (2 H, m, 2 CH), and 5.57 [1 H, td, CHF_2 , $J_{HF}(gem)$ 54, $J_{HF}(vic)$ 7.2 Hz], low field from external tetramethylsilane; δ_F 50.6 [2 F, dd, CHF_2 , $J_{FF}(vic)$ 9 Hz], and 154.3 (1 F, m, CF), high field from external trifluoroacetic acid; and 1-fluoro-r-1-difluoromethyl-c-2,3-dimethylcyclopropane (10b) (0.74 g, 5.4 mmol, 27%) (Found: C, 52.2; H, 6.7%; M^+ , 138), b.p. (Siwoloboff) 90 °C; m/e (4%, M^+), 123 (9, $[M - CH_3]^+$), 87 (100, $[M - CHF_2]^+$), 57 (84, $C_3H_2F^+$), 51 (25%, CHF_2^+), and 41 (78%, $C_3H_5^+$); δ_H 0.86 (6 H, m, 2 CH_3), 1.2–1.4 (2 H, m, 2 CH), and 5.50 [1 H, td, CHF_2 , $J_{HF}(gem)$ 52, $J_{HF}(vic)$ 16.2 Hz], low field from external tetramethylsilane; δ_F 51.4 [2 F, dd, CHF_2 , $J_{FF}(vic)$ 12 Hz], and 119.8 (1 F, m, CF), high field from external trifluoroacetic acid.

(f) *With trans-but-2-ene*. A mixture of the silane (1.86 g, 10 mmol) and the olefin (8.31 g, 148.4 mmol), heated at 150 °C (18 h), gave (i) a mixture of silicon tetrafluoride (1.02 g, 9.8 mmol, 98%) and trifluoroethylene (0.09 g, 1.1 mmol, 11%); (ii) unchanged *trans-but-2-ene* (7.76 g, 1.386 mmol, 93% recovered); and (iii) a liquid mixture (1.18 g) which was separated by g.l.c. (2 m D.N.P. at 60 °C) into its components (3) (0.01 g, 0.05 mmol, 1%); and 1-fluoro-r-1-difluoromethyl-c-2-t-3-dimethylcyclopropane (10c) (1.17 g, 8.5 mmol, 85%) (Found: C, 52.4; H, 6.7%; M^+ , 138. $C_6H_9F_3$ requires C, 52.2; H, 6.5%; M , 138), b.p. (Siwoloboff) 88 °C; m/e 138 (6%, M^+), 123 (5, $[M - CH_3]^+$), 87 (100, $[M - CHF_2]^+$), 57 (52%, $C_3H_2F^+$), 51 (33%, CHF_2^+), and 41 (81%, $C_3H_5^+$); δ_H 0.80–0.94 (8 H, complex, 2 CHMe) and 5.50 [1 H, td, CHF_2 , $J_{HF}(gem)$ 53.7, $J_{HF}(vic)$ 12.8 Hz], low field from external tetramethylsilane; δ_F 46.1 [1 F, ddd, CHF_A , $J_{FAFB}(gem)$ 292, $J_{FFA}(vic)$ 10 Hz], 50.6 [1 F, ddd, CHF_B , $J_{FFB}(vic)$ 11 Hz], and 137.1 (1 F, m, CF), high field from external trifluoroacetic acid.

(g) *With 2-methylbut-2-ene*. A mixture of the silane (3.72 g, 20 mmol) and the olefin (9.8 g, 140 mmol), heated at 150 °C (18 h), gave (i) a mixture of silicon tetrafluoride (2.0 g, 19.2 mmol, 96%) and trifluoroethylene (0.26 g, 3.2 mmol, 16%); (ii) unchanged 2-methylbut-2-ene (7.50 g, 107.1 mmol, 76% recovered); and (iii) a liquid mixture (2.43 g)

which was separated by g.l.c. (2 m D.N.P. at 80 °C) into its components (3) (trace); 1-fluoro-r-1-difluoromethyl-c-2-t-2,3-trimethylcyclopropane (11a) (1.41 g, 9.3 mmol, 47%) (Found: C, 55.6; H, 7.4%; M^+ , 152. $C_7H_{11}F_3$ requires C, 55.3; H, 7.2%; M , 152), b.p. (Siwoloboff) 109 °C; m/e 152 (7%, M^+), 137 (41, $[M - CH_3]^+$), 117 (6, $C_6H_7F_2^+$), 101 (100, $[M - CHF_2]^+$), 73 (63, $C_4H_6F^+$), and 51 (22%, CHF_2^+); δ_H 0.90 (9 H, s, 3 CH_3), 0.96 (1 H, CH), and 5.54 [1 H, td, CHF_2 , $J_{HF}(gem)$ 53.5, $J_{HF}(vic)$ 13.9 Hz], low field from external tetramethylsilane; δ_F 46.6 [1 F, ddd, $CHFF_A$, $J_{FAFB}(gem)$ 292, $J_{FFA}(vic)$ 10 Hz], 49.3 [1 F, ddd, $CHFF_B$, $J_{FFB}(vic)$ 12 Hz], and 146.2 (1 F, m, CF), high field from external trifluoroacetic acid; and 1-fluoro-r-1-difluoromethyl-c-2,3-t-2-trimethylcyclopropane (11b) (1.02 g, 6.7 mmol, 34%) (Found: C, 55.6; H, 7.4%; M^+ , 152), b.p. (Siwoloboff) 111 °C; m/e 152 (5%, M^+), 137 (44, $[M - CH_3]^+$), 117 (6%, $C_6H_7F_2^+$), 101 (100, $[M - CHF_2]^+$), 73 (63%, $C_4H_6F^+$), and 51 (22%, CHF_2^+); δ_H 0.90 (9 H, s, 3 CH_3), 1.24 (1 H, CH), and 5.54 [1 H, td, CHF_2 , $J_{HF}(gem)$ 52, $J_{HF}(vic)$ 17.2 Hz], low field from external tetramethylsilane; δ_F 50.3 [2 F, dd, CHF_2 , $J_{FF}(vic)$ 13 Hz], and 133.3 (1 F, m, CF), high field from external trifluoroacetic acid.

A high-boiling residue (ca. 0.2 g) was extracted from the reaction bulb with ether; this was not examined further.

(h) *With 2,3-dimethylbut-2-ene*. A mixture of the silane (3.72 g, 20 mmol) and the olefin (16.81 g, 200 mmol), heated at 150 °C (16 h), gave (i) a mixture of silicon tetrafluoride (2.02 g, 19.8 mmol, 99%) and trifluoroethylene (0.10 g, 1.2 mmol, 6%); (ii) unchanged olefin (14.76 g, 176 mmol, 88% recovered); and (iii) 1-fluoro-1-difluoromethyl-2,2,3,3-tetramethylcyclopropane (12) (2.85 g, 17.2 mmol, 86%) (Found: C, 58.0; H, 7.9%; M^+ , 166. $C_8H_{13}F_3$ requires C, 57.8; H, 7.8%; M , 166), b.p. (Siwoloboff) 135 °C; m/e 166 (8%, M^+), 115 (33, $[M - CHF_2]^+$), 84 (30, $C_6H_{12}^+$), 73 (21, $C_4H_6F^+$), 69 (79, $C_5H_9^+$), 61 (27, $C_3H_6F^+$), 55 (33, $C_4H_7^+$), 41 (100, $C_3H_5^+$), 39 (39, $C_3H_3^+$), 32 (21, CHF^+), and 28 (88, $C_2H_4^+$); δ_H 0.83 [1 H, td, CHF_2 , $J_{HF}(gem)$ 54, $J_{HF}(vic)$ 18 Hz], and 5.52 [1 H, d, 4 CH_3], high field from external benzene; δ_F 50.2 [2 F, dd, CHF_2 , $J_{FF}(vic)$ 13 Hz], and 146.0 (1 F, q, CF), high field from external trifluoroacetic acid.

(i) *With cyclohexene*. A mixture of the silane (3.72 g, 20 mmol) and cyclohexene (15.4 g, 190 mmol), heated at 150 °C (16 h), gave (i) a mixture of silicon tetrafluoride (2.04 g, 19.6 mmol, 98%) and trifluoroethylene (0.55 g, 6.7 mmol, 33%); (ii) unchanged cyclohexene (12.59 g, 152.5 mmol, 81% recovered) contaminated with (3) (ca. 0.07 g, 0.4 mmol, 4%); and (iii) a liquid mixture (2.0 g) which was separated by g.l.c. (2 m D.N.P. at 100 °C) into its components; endo-7-fluoro-7-difluoromethylbicyclo[4.1.0]heptane (13a) (1.46 g, 8.9 mmol, 45%) (Found: C, 58.4; H, 6.9%; M^+ , 164. $C_8H_{11}F_3$ requires C, 58.5; H, 6.8%; M , 164), b.p. (Siwoloboff) 152 °C; m/e 164 (12%, M^+), 122 (69, $C_5H_5F_3^+$), 113 (42, $[M - CHF_2]^+$), 93 (12, $C_7H_9^+$), 85 (30, $C_5H_6F^+$), 81 (46, $C_6H_9^+$), 77 (20, $C_6H_5^+$), 68 (100, $C_5H_8^+$), 65 (11, $C_5H_5^+$), 59 (21, $C_3H_4F^+$), 55 (85, $C_4H_7^+$), 51 (21, CHF_2^+), 41 (34, $C_3H_5^+$), and 39 (39, $C_3H_3^+$); δ_H 1.41 [1 H, dt, CHF_2 , $J_{HF}(gem)$ 54.0, $J_{HF}(vic)$ 7.8 Hz] and 5.38–5.75 (10 H, br, ring CH_2 and CH), high field from external *p*-dichlorobenzene; δ_F 51.8 [2 F, dd, CHF_2 , $J_{FF}(vic)$ 10 Hz] and 149.5 (1 F, m, CF), high field from external trifluoroacetic acid; and exo-7-fluoro-7-difluoromethylbicyclo[4.1.0]heptane (13b) (0.54 g, 3.3 mmol, 17%), b.p. (Siwoloboff) 159–160 °C; m/e 164 (4%, M^+), 122 (69, $C_5H_5F_3^+$), 113 (42, $[M - CHF_2]^+$), 93 (14, $C_7H_9^+$), 85 (31, $C_5H_6F^+$), 81

(45, $C_6H_9^+$), 77 (23, $C_6H_5^+$), 68 (100, $C_6H_8^+$), 65 (12, $C_5H_5^+$), 59 (23, $C_3H_4F^+$), 55 (94, $C_4H_7^+$), 51 (23, CHF_2^+), 41 (40, $C_3H_5^+$), and 39 (46, $C_3H_3^+$); δ_H 1.20 [1 H, dt, CHF_2 , $J_{HF}(gem)$ 52.0, $J_{HF}(vic)$ 18 Hz] and 5.38–5.75 (10 H, br, ring CH_2 and CH), high field from external *p*-dichlorobenzene; δ_F 52.3 [2 F, dd, CHF_2 , $J_{FF}(vic)$ 12 Hz] and 120.0 (1 F, m, CF), high field from external trifluoroacetic acid; the product was contaminated with a trace quantity of cyclohexane.

A residual tar (0.13 g) remained in the reaction vessel; this was not examined further.

Reaction of (1,1,2,2-Tetrafluoroethyl)trifluorosilane with Tris(trifluoromethyl)phosphine.—A mixture of the silane (3.72 g, 20.0 mmol) and the phosphine (47.59 g, 0.20 mol), heated in a Pyrex ampoule (*ca.* 250 cm³) at 150 °C (5 h), gave (i) a mixture of silicon tetrafluoride (1.98 g, 19.0 mmol, 95%) and trifluoroethylene (0.25 g, 3.0 mmol, 15%); (ii) unchanged phosphine (43.28 g, 0.182 mol, 91% recovered); (iii) 1,2,2-trifluoroethylidenetri(trifluoromethyl)phosphorane (14) (2.37 g, 7.4 mmol, 37%) (Found: C, 18.5; H, 0.55%. C_5HF_9P requires C, 18.75; H, 0.3%); i.r., λ_{max} 6.02 μ m; m/e 263 (5%, $[M - CF_4]^+$), 262 (4, $[M - CHF_4]^+$), and 69 (100, CF_3^+); δ_H 0.46 (ddm), low field from external benzene; (iv) a higher-boiling unidentified yellow oil (0.43 g); and (v) tar (0.3 g).

Pyrolyses.—(a) *A mixture of 1-fluoro-r-1-difluoromethyl-t-2-methylpropane (8a) and 1-fluoro-r-1-difluoromethyl-c-2-methylcyclopropane (8b).* (i) At 710 °C. A mixture of (8a) (0.232 g, 1.87 mmol) and (8b) (0.143 g, 1.15 mmol) was flow-pyrolysed (contact time 0.15 s) and the product was immediately passed over potassium hydroxide pellets and collected *in vacuo* at –196 °C. Analysis of the product gave (i) a trace of a gaseous product, (ii) a liquid mixture which was separated by g.l.c. (2 m D.N.P. at 50 °C) into its components, unchanged (8a) (0.114 g, 0.92 mmol, 49% recovered); unchanged (8b) (0.114 g, 0.92 mmol, 80% recovered); 2-difluoromethylbuta-1,3-diene (18) (0.088 g, 0.84 mmol, 71%) (Found: M^+ , 104. Calc. for $C_5H_6F_2$: M , 104); i.r., λ_{max} (liquid) 3.24 (C–H str), 5.97 and 6.12 (C=C str) μ m; m/e 104 (64%, M^+), 85 (10, $C_5H_6F^+$), 53 (100, $[M - CHF_2]^+$), and 51 (42, CHF_2^+); δ_H 1.30 (1 H, dd, H^2 , $J_{2,4}$ 18, $J_{2,3}$ 11 Hz), 2.14 (1 H, H^4), 2.23 (1 H, H^5), 2.31 (1 H, H^6), 2.43 (1 H, H^3), and 1.47 [1 H, t, CHF_2 , $J_{HF}(gem)$ 55 Hz], high field from external *p*-dichlorobenzene; δ_F 40.8 (d, CHF_2), high field from external trifluoroacetic acid; and at least seven minor products (*ca.* 0.027 g), two of which were identified as *cis*- and *trans*-1,2-difluoropenta-1,4-diene (24) (*ca.* 2.5 and 1.5%, respectively) (Found: M^+ , 104. Calc. for $C_5H_6F_2$: M , 104) on the basis of their g.l.c. retention times and mass spectra.

(ii) At 750 °C. A mixture of (8a) (0.248 g, 2.0 mmol) and (8b) (0.153 g, 1.23 mmol) when flow-pyrolysed at 750 °C (contact time 0.12 s) and the product passed over potassium hydroxide pellets, gave (i) a gaseous product (<0.1 mmol) and (ii) a mixture of unchanged (8a) (0.003 g, 0.03 mmol, 1.5% recovered), unchanged (8b) (0.081 g, 0.78 mmol, 63% recovered), (18) (0.214 g, 2.06 mmol, 85%), and at least seven minor products (0.026 g), two of which were identified as the *cis*- and *trans*-isomers of the 1,4-diene (24) (*ca.* 2 and 1.5% respectively).

(b) *1-Fluoro-1-difluoromethyl-2,2-dimethylcyclopropane (9).*—(i) At 685 °C. 1-Fluoro-1-difluoromethyl-2,2-dimethylcyclopropane (9) (0.620 g, 4.49 mmol), on flow-pyrolysis at 685 °C (contact time 0.20 s), gave (i) a mixture of silicon tetrafluoride (0.021 g, 0.20 mmol, 18%) and unidentified

gaseous product (0.05 mmol); (ii) a liquid mixture which was separated by g.l.c. (2 m D.N.P. at 60 °C) into its components, unchanged (9) (0.388 g, 2.81 mmol, 62% recovered); 2-difluoromethyl-3-methylbuta-1,3-diene (19) (0.035 g, 0.30 mmol, 18%) (Found: C, 60.1; * H, 7.0%; M^+ , 118. $C_6H_8F_2$ requires C, 61.0; H, 6.8%; M , 118), i.r., λ_{max} (liquid) 3.23 (C–H str), and 6.03 and 6.18 (C=C str) μ m; m/e 118 (100%, M^+), 103 (71, $[M - CH_3]^+$), 67 (83, $[M - CHF_2]^+$), and 51 (36%, CHF_2^+); δ_H 1.38 (3 H, s, CH_3), 4.48 (1 H, H^3), 4.70 (1 H, H^6), 4.87 (1 H, H^5), 4.98 (1 H, H^4), and 5.70 [1 H, t, CHF_2 , $J_{HF}(gem)$ 55 Hz], low field from external tetramethylsilane; δ_F 37.3 (d, CHF_2), high field from external trifluoroacetic acid; and trace amounts of three compounds which remain unidentified; (iii) higher-boiling material, possibly a polymer of diene (19) (0.095 g, 41% by weight) (Found: C, 60.3; H, 6.7%), and (iv) tar (0.007 g).

(ii) At 700 °C. The results obtained from two further flow-pyrolyses of cyclopropane (9) at 700 °C (contact times *ca.* 0.20 s) are given in Table 3.

(c) *1-Fluoro-r-1-difluoromethyl-c-2-t-3-dimethylcyclopropane (10c).* (i) At 690 °C. 1-Fluoro-r-1-difluoromethyl-c-2-t-3-dimethylcyclopropane (10c) (0.449 g, 3.24 mmol), on flow-pyrolysis at 690 °C (contact time 0.18 s), gave (i) a mixture of silicon tetrafluoride (0.047 g, 0.45 mmol, 56%) and unidentified gaseous product (0.03 mmol); (ii) a liquid mixture which was separated by g.l.c. (2 m D.N.P. at 60 °C) into its components, unchanged (10c) (0.157 g, 1.13 mmol, 35% recovered); *cis*-3-difluoromethylpenta-1,3-diene (20), (0.111 g, 0.94 mmol, 45%) (Found: C, 57.0; * H, 6.7%; M^+ , 118. $C_6H_8F_2$ requires C, 61.0; H, 6.8%; M , 118); i.r., λ_{max} (liquid) 3.23 (C–H str), 5.98 (s), 6.03 and 6.13 (C=C str); m/e 118 (51%, M^+), 103 (23, $[M - CH_3]^+$), 67 (100, $[M - CHF_2]^+$), and 51 (25, CHF_2^+); δ_H 1.33 (3 H, m, CH_3), 4.76 (1 H, H^3), 5.02 (1 H, H^4), 5.49 (1 H, H^6), 5.60 [1 H, t, CHF_2 , $J_{HF}(gem)$ 55.5 Hz], and 6.02 (1 H, dd, H^2 , $J_{2,3}$ 11, $J_{2,4}$ 18 Hz), low field from external tetramethylsilane; δ_F 35.6 (d, CHF_2), high field from external trifluoroacetic acid; and seven minor products (*ca.* 0.020 g), two of which were identified as the cyclopropanes (10a) (*ca.* 1.5%) and (10b) (*ca.* 1%) (Found: M^+ , 138. Calc. for $C_6H_9F_3$: M , 138) on the basis of their g.l.c. retention times and mass spectra, and three of which were tentatively identified as *cis*- and *trans*-1,2-difluoro-3-methylpenta-1,4-diene (25) (*ca.* 1% each) (Found: M^+ , 118. Calc. for $C_6H_8F_2$: M , 118) and 1-fluoro-2-vinylbuta-1,3-diene (26) (*ca.* 2%) (Found: M^+ , 98. Calc. for C_6H_7F : M , 98); m/e 98 (49%, M^+), 97 (100, $C_5H_6F^+$), 77 (28, $C_6H_5^+$), and 32 (43, CHF^+); δ_F 51.5 [d, $=CHF$, $J_{HF}(gem)$ 78 Hz], high field from external trifluoroacetic acid; (iii) polymeric material (0.038 g, 10%); and (iv) a tar (0.063 g).

(ii) At 705 °C. A second flow-pyrolysis of cyclopropane (10c) at 705 °C (contact time 0.24 s) gave the results shown in Table 3.

(d) *A mixture of 1-fluoro-r-1-difluoromethyl-t-2,3-dimethylcyclopropane (10a) and 1-fluoro-r-1-difluoromethyl-c-2,3-dimethylcyclopropane (10b).* A mixture of the cyclopropanes (10a) (0.252 g, 1.82 mmol) and (10b) (0.126 g, 0.91 mmol), flow-pyrolysed at 700 °C (contact time 0.18 s) and the product passed over potassium hydroxide pellets, gave (i) gaseous product (<0.1 mmol), and (ii) a liquid mixture (0.329 g) which was shown by g.l.c. (4 m D.N.P. at 80 °C) to consist of unchanged (10a) (0.046 g, 0.33 mmol, 18% recovered), unchanged (10b) (0.069 g, 0.50 mmol, 55% recovered), (20) (0.182 g, 1.54 mmol, 81%), triene (26) (*ca.*

0.012 g, 0.12 mmol, 6%), the *cis*- and *trans*-isomer of dienes (25) (*ca.* 3 and 2%, respectively), and an unidentified component (*ca.* 4%).

(e) A mixture of 1-fluoro-*r*-1-difluoromethyl-*c*-2-*t*-2,3-trimethylcyclopropane (11a) and 1-fluoro-*r*-1-difluoromethyl-*c*-2,3-*t*-2-trimethylcyclopropane (11b). (i) At 270 °C. A mixture of (11a) (0.221 g, 1.46 mmol) and (11b) (0.160 g, 1.05 mmol), on static pyrolysis at 270 °C (20 h), gave (i) silicon tetrafluoride (0.035 g, 0.34 mmol, 87%), (ii) a liquid mixture which was separated by g.l.c. (2 m D.N.P. at 80 °C) into its components, unchanged (11a) (0.048 g, 0.32 mmol, 22% recovered), unchanged (11b) (0.053 g, 0.35 mmol, 33% recovered), *cis*-1,2-difluoro-3,4-dimethylpenta-1,4-diene (16a) (0.138 g, 1.05 mmol, 57%) (Found: C, 63.9; H, 7.8%; M^+ , 132. $C_7H_{10}F_2$ requires C, 63.6; H, 7.6%; M , 132); m/e 132 (11%, M^+), 117 (100, $[M - CH_3]^+$), 97 (47, $C_6H_6F^+$), 77 (45, $C_6H_5^+$), and 41 (86, $C_3H_5^+$); δ_H 1.20 [1 H, dd, =CHF, $J_{HF}(gem)$ 74, $J_{HF}(trans)$ 17 Hz], 2.58 (2 H, m, CH_2), 4.65 (1 H, m, CH), 5.72 (3 H, s, CH_3), and 6.27 [3 H, d, CH_3 , $J_{H-CH_3}(vic)$ 7 Hz], high field from external *p*-dichlorobenzene; δ_F 63.0 [1 F, dd, CF, $J_{FF}(cis)$ 10 Hz], and 90.9 [1 F, dd, =CHF], high field from external trifluoroacetic acid, *trans*-1,2-difluoro-3,4-dimethylpenta-1,4-diene (16b) (0.057 g, 0.43 mmol, 23%) (Found: C, 63.9; H, 7.8%; M^+ , 132); m/e 132 (40%, M^+), 117 (93, $[M - CH_3]^+$), 97 (48, $C_6H_6F^+$), 77 (48, $C_6H_5^+$), and 41 (100, $C_3H_5^+$); δ_H 0.50 [1 H, dd, =CHF, $J_{HF}(gem)$ 76, $J_{HF}(cis)$ 5 Hz], 2.58 (2 H, m, CH_2), 4.10 (1 H, m, CH), 5.69 (3 H, s, CH_3), and 6.19 [3 H, d, CH_3 , $J_{H-CH_3}(vic)$ 8 Hz], high field from external *p*-dichlorobenzene; δ_F 91.5 [1 F, dd, CF, $J_{FF}(trans)$ 127.6 Hz], and 105.9 [1 F, dd, =CHF], high field from external trifluoroacetic acid [i.r. *cis-trans* mixture (liquid), λ_{max} 3.21, 3.26 (C-H str), 5.84 and 6.04 (C=C str) μm]; 1-fluoro-3-methyl-2-vinylbuta-1,3-diene (27) (0.005 g, 0.04 mmol, 2%), and three minor products (*ca.* 0.008 g), one of which was tentatively identified as *trans*-3-difluoromethyl-2-methylpenta-1,3-diene (21b) (*ca.* 1.5%) (Found: M^+ , 132. Calc. for $C_7H_{10}F_2$: M , 132); and (iii) a tar (<0.03 g). A small amount of water was also present in the product mixture.

(ii) At 720 °C. A mixture of cyclopropanes (11a) (0.269 g, 1.77 mmol) and (11b) (0.195 g, 1.28 mmol), passed through the pyrolysis tube at 720 °C (contact time 0.21 s) and the product treated with potassium hydroxide pellets, gave (i) a trace of gaseous product, and (ii) a liquid mixture which was separated by g.l.c. (2 m D.N.P. at 80 °C) into its components, 1-fluoro-3-methyl-2-vinylbuta-1,3-diene (27) (0.128 g, 1.14 mmol, 37%) (Found: C, 71.8; H, 8.6%; M^+ , 112. C_7H_9F requires C, 74.9; H, 8.0%; M , 112), i.r., λ_{max} (liquid) 3.25 (C-H str), and 5.84, 6.03, and 6.06 (C=C str) μm ; m/e 112 (42%, M^+), 97 (100, $[M - CH_3]^+$), and 77 (34, $C_6H_5^+$); δ_H 1.08 [1 H, d, =CHF, $J_{HF}(gem)$ 82 Hz], 1.28 (1 H, H^2), 2.25 (1 H, H^4), 2.48 (1 H, H^5), 2.52 (1 H, H^3), 2.67 (1 H, H^6), and 5.74 (3 H, m, CH_3), high field from external *p*-dichlorobenzene; δ_F 52.8 (d, =CHF), high field from external trifluoroacetic acid; *cis*-3-difluoromethyl-2-methylpenta-1,3-diene (21a) (0.162 g, 1.23 mmol, 40%) (Found: C, 26.6, H, 7.5%; M^+ , 132. $C_7H_{10}F_2$ requires C, 63.6; H, 7.6%; M , 132), i.r., λ_{max} (liquid) 3.25 (C-H str), and 6.02 and 6.10 (C=C str) μm ; m/e 132 (100%, M^+), 117 (35, $[M - CH_3]^+$), 97 (40, $C_6H_6F^+$), 81 (72, $[M - CHF_2]^+$), and 51 (31%, CHF_2^+); δ_H 1.66 [1 H, t, CHF_2 , $J_{HF}(gem)$ 55 Hz], 1.74 (1 H, H^6), 2.40 (1 H, H^4), 2.66 (1 H, H^3), 5.67 (3 H, s, CH_3), and 5.86 (3 H, m, CH_3), high field from external *p*-dichlorobenzene; δ_F 34.2 (d, CHF_2), high field from external trifluoroacetic acid; 3-difluoromethyl-4-methylpenta-1,3-diene

(22) (0.040 g, 0.30 mmol, 10%) (Found: M^+ , 132. Calc. for $C_7H_{10}F_2$: M , 132); i.r., λ_{max} (liquid) 3.24 (C-H str), and 6.04 and 6.07 (C=C str) μm ; m/e 132 (100%, M^+), 117 (39, $[M - CH_3]^+$), 97 (47, $C_6H_6F^+$), 81 (79, $[M - CHF_2]^+$), and 51 (34, CHF_2^+); δ_H 1.06 [1 H, t, CHF_2 , $J_{HF}(gem)$ 54 Hz], 1.58 (1 H, H^2), 2.42 (1 H, H^4), 2.65 (1 H, H^3), and 5.69 (6 H, br, 2 CH_3), high field from external *p*-dichlorobenzene; δ_F 36.2 (d, CHF_2), high field from external trifluoroacetic acid; a product which was tentatively identified as *trans*-3-difluoromethyl-2-methylpenta-1,3-diene (21b) (0.029 g, 0.22 mmol, 7%) (Found: M^+ , 132. Calc. for $C_7H_{10}F_2$: M , 132); m/e 132 (92%, M^+), 117 (46, $[M - CH_3]^+$), 97 (79, $C_6H_6F^+$), 81 (100, $[M - CHF_2]^+$), 77 (52, $C_6H_5^+$), and 51 (45, CHF_2^+); and at least seven minor products (*ca.* 0.014 g) which remain unidentified.

(f) 1-Fluoro-1-difluoromethyl-tetramethylcyclopropane (12). (i) At 270 °C. 1-Fluoro-1-difluoromethyltetramethylcyclopropane (12) (0.409 g, 2.41 mmol), on static pyrolysis at 270 °C (20 h), gave (i) silicon tetrafluoride (0.052 g, 0.5 mmol, 83%); (ii) a liquid mixture which was separated by g.l.c. (2 m D.N.P. at 100 °C) into its components, *cis*-1,2-difluoro-3,3,4-trimethylpenta-1,4-diene (17a) (0.192 g, 1.33 mmol, 55%) (Found: C, 65.6; H, 8.4%; M^+ , 146. $C_8H_{12}F_2$ requires C, 65.7; H, 8.2%; M , 146); m/e 146 (8%, M^+), 131 (100, $[M - CH_3]^+$), 111 (33, $C_7H_8F^+$), and 41 (92, $C_3H_5^+$); δ_H 1.15 [1 H, dd, =CHF, $J_{HF}(gem)$ 74, $J_{HF}(trans)$ 17 Hz], 2.57 (2 H, m, = CH_2), 5.68 (3 H, s, CH_3), and 6.18 (6 H, s, CMe_2), high field from external *p*-dichlorobenzene; δ_F 139.8 [1 F, dd, CF, $J_{FF}(cis)$ 8 Hz] and 172.0 (1 F, dd, =CHF), high field from internal trichlorofluoromethane; *trans*-1,2-difluoro-3,3,4-trimethylpenta-1,4-diene (17b) (0.128 g, 0.89 mmol, 37%) (Found: C, 65.6; H, 8.4%; M^+ , 146. $C_8H_{12}F_2$ requires C, 65.7; H, 8.2%; M , 146); m/e 146 (24%, M^+), 131 (95, $[M - CH_3]^+$), 111 (21, $C_7H_8F^+$), and 41 (100, $C_3H_5^+$); δ_H 0.51 [1 H, dd, =CHF, $J_{HF}(gem)$ 76, $J_{HF}(cis)$ 8 Hz], 2.57 (2 H, m, = CH_2), 5.68 (3 H, s, CH_3), and 6.07 (6 H, CMe_2), high field from external *p*-dichlorobenzene; δ_F 162.7 [1 F, dd, CF, $J_{FF}(trans)$ 128 Hz] and 180.0 (1 F, dd, =CHF), high field from internal trichlorofluoromethane, [i.r. *cis-trans* mixture (liquid), λ_{max} 3.20 and 3.24 (C-H str), and 5.86 and 6.05 (C=C str) μm]; and (23) (<1%); and (iii) a tar (<0.05 g). A small amount of water was also detected in the products.

(ii) At 680 °C. Cyclopropane (12) (0.34 g, 2.05 mmol), flow-pyrolysed at 680 °C (contact time 0.24 s), gave (i) gaseous product (<0.1 mmol), and (ii) a liquid mixture which was separated by g.l.c. (2 m D.N.P. at 100 °C) into its components, unchanged (12) (0.015 g, 0.09 mmol, 4% recovered); 1-fluoro-3-methyl-2-isopropenylbuta-1,3-diene (28) (0.067 g, 0.53 mmol, 27%) (Found: C, 72.5; H, 8.9%; M^+ , 126. $C_8H_{11}F$ requires C, 76.2; H, 8.7%; M , 126); i.r., λ_{max} (liquid) 3.24 (C-H str), and 5.85 and 6.05 (C=C str) μm ; m/e 126 (35%, M^+), 111 (100, $[M - CH_3]^+$), and 91 (45, $C_7H_7^+$); δ_H 1.09 [1 H, d, =CHF, $J_{HF}(gem)$ 83 Hz], 2.54—2.84 (4 H, m, H^3 , H^4 , H^5 , H^6), 5.76 (3 H, s, CH_3), and 5.83 (3 H, CH_3), high field from external *p*-dichlorobenzene; δ_F 51.5 (d, =CHF), high field from external trifluoroacetic acid; 3-difluoromethyl-2,4-dimethylpenta-1,3-diene (23) (0.178 g, 1.27 mmol, 65%) (Found: C, 62.4; H, 8.6%; M^+ , 146. $C_8H_{12}F_2$ requires C, 65.7; H, 8.2%; M , 146); i.r., λ_{max} (liquid) 3.24 (C-H str) and 6.06 (C=C str) μm ; m/e 146 (100%, M^+), 131 (43, $[M - CH_3]^+$), 111 (49, $C_7H_8F^+$), 95 (41, $[M - CHF_2]^+$), and 51 (28%, CHF_2^+); δ_H 1.04 [1 H, t, CHF_2 , $J_{HF}(gem)$ 56 Hz], 2.41 (1 H, H^4), 2.77 (1 H, H^3) and 5.70 [9 H, br, 3 CH_3], high field from external *p*-dichloro-

benzene; δ_F 35.1 (d, CHF_2), high field from external trifluoroacetic acid; and five minor products (0.014 g) two of which possessed the same g.l.c. retention times as *cis*- and *trans*-1,2-difluoro-3,3,4-trimethylpenta-1,3-diene (17a and b) (*ca.* 1 and 0.5%, respectively).

(iii) At 720 °C. A further flow pyrolysis of cyclopropane (12) at 720 °C (contact time 0.21 s) gave the results shown in Table 3.

(g) A mixture of *cis*- and *trans*-1,2-difluoro-3,3,4-trimethylpenta-1,4-diene (17). (i) At 680 °C. A mixture of *cis*- and *trans*-1,2-difluoro-3,3,4-trimethylpenta-1,4-diene (17) (0.18 g, 1.23 mmol), flow-pyrolysed at 680 °C (contact time 0.17 s), gave a liquid mixture which was shown by g.l.c. (2 m D.N.P. at 100 °C) to consist of unchanged (17) (0.171 g, 1.17 mmol, 95% recovered), 3-difluoromethyl-2,4-dimethylpenta-1,3-diene (23) (*ca.* 1% conversion), and four minor products (*ca.* 0.006 g) which remain unidentified.

(ii) At 720 °C. A mixture of the *cis*- and *trans*-1,4-dienes (17) (0.17 g, 1.17 mmol), flow-pyrolysed at 725 °C (contact time 0.28 s), gave a complex liquid mixture (0.12 g) which was shown by g.l.c. (2 m D.N.P. at 75 °C) to contain trace quantities of triene (28) (Found: M^+ , 126. Calc. for $\text{C}_8\text{H}_{11}\text{F}$: M , 126) and (23) (Found: M^+ , 146. Calc. for $\text{C}_8\text{H}_{12}\text{F}_2$: M , 146), together with at least *ten* other products which remain unidentified. A g.l.c. (as above)-mass spectrometric examination of the products indicated the presence of compounds of molecular formulae $\text{C}_8\text{H}_{11}\text{F}$ (Found: M^+ , 126. Calc. for $\text{C}_8\text{H}_{11}\text{F}$: M , 126), $\text{C}_7\text{H}_{10}\text{F}_2$ (Found: M^+ , 132. Calc. for $\text{C}_7\text{H}_{10}\text{F}_2$: M , 132), $\text{C}_6\text{H}_8\text{F}_2$ (Found: M^+ , 118. Calc. for $\text{C}_6\text{H}_8\text{F}_2$: M , 118), C_8H_{10} (Found: M^+ , 106. Calc. for C_8H_{10} : M , 106), and $\text{C}_5\text{H}_6\text{F}_2$ (Found: M^+ , 104. Calc. for $\text{C}_5\text{H}_6\text{F}_2$: M , 104). The i.r. spectrum of the liquid mixture showed broad absorptions at λ_{max} 3.25 (C-H str), and 5.89, 6.03, and 6.08 (C=C str) μm ; the ^1H n.m.r. spectrum of the mixture was complex and showed main broad absorptions at δ 0.01, 2.1–2.5 (olefinic CH), 5.2 (=C- CH_3), and 5.45 (=C- CH_3), high field from external *p*-dichlorobenzene.

(iii) At 680 °C in the presence of silicon tetrafluoride. A mixture of *cis*- and *trans*-1,4-dienes (17) (0.14 g, 0.98 mmol) and silicon tetrafluoride (0.52 g, 5.0 mmol), flow-pyrolysed at 680 °C (contact time 0.15 s), gave (i) unchanged silicon tetrafluoride (0.49 g, 4.7 mmol, 94% recovered), and (ii) a liquid mixture which was shown by g.l.c. (2 m D.N.P. at 100 °C) to consist of unchanged (17) (0.13 g, 0.89 mmol, 93% recovered) contaminated with five minor products, two of which possessed the same g.l.c. retention times as (28) and (23).

(h) 1,2,2,3,3-Pentafluoro-1-difluoromethylcyclopropane (6). (i) Alone. The cyclopropane (6) (0.455 g, 2.50 mmol), on static pyrolysis at 200 °C (320 h), gave (i) carbon monoxide (0.032 g, 1.15 mmol, 46%), (ii) a mixture of silicon tetrafluoride (0.061 g, 0.59 mmol, 47%) and tetrafluoroethylene (0.038 g, 0.38 mmol, 30%); (iii) hexafluorocyclopropane (4) (0.020 g, 0.013 mmol, 16%); (iv) octafluorocyclobutane (0.008 g, 0.004 mmol, 6%); and (v) 3*H*-pentafluoropropene (5) (0.328 g, 2.475 mmol, 99%) (Found: C, 27.3; H, 0.9%; M , 132. Calc. for C_3HF_5 : C, 27.3; H, 0.8%; M , 132), b.p. (isoteniscope) 1.3 ± 0.5 °C (lit.,¹⁸ 1.8 °C).

At 150 °C (16 h) the cyclopropane (6) (93%) was recovered unchanged, but at 300 °C (160 h) the cyclopropane (6) (0.454 g, 2.50 mmol), gave (i) carbon monoxide (0.035 g, 1.25 mmol, 50%); (ii) a mixture of silicon tetrafluoride (0.046 g, 0.62 mmol, 49%) and tetrafluoroethylene (0.035 g, 0.35 mmol, 28%); (iii) (4) (0.008 g, 0.06 mmol, 6%); (iv)

octafluorocyclobutane (0.015 g, 0.075 mmol, 12%); and (v) (5) (0.330 g, 2.50 mmol, 100%).

A series of decompositions of the cyclopropane carried out under the same conditions as a series of preparations of the cyclopropane are compared in the Discussion section.

(ii) In the presence of glass wool. The cyclopropane (6) (0.453 g, 2.49 mmol), on static pyrolysis at 200 °C (320 h) in a Pyrex tube packed with dried (150 °C, 1 h) and degassed glass wool, gave (i) carbon monoxide (0.069 g, 2.47 mmol, 99%); (ii) a mixture of silicon tetrafluoride (0.129 g, 1.235 mmol, 99%) and tetrafluoroethylene (trace); and (iii) (5) (0.329 g, 2.49 mmol, 100%).

(iii) In the presence of cyclohexene. A mixture of the cyclopropane (6) (0.456 g, 2.51 mmol) and cyclohexene (2.052 g, 25.0 mmol), on static pyrolysis at 200 °C (320 h), gave (i) carbon monoxide (0.008 g, 0.28 mmol, 11%); (ii) a mixture of silicon tetrafluoride (0.017 g, 0.16 mmol, 13%) and tetrafluoroethylene (0.018 g, 0.18 mmol, 14%); (iii) octafluorocyclobutane (trace); (iv) 3*H*-pentafluoropropene (0.326 g, 2.48 mmol, 99%); (v) unchanged cyclohexene (1.825 g, 22.25 mmol, 89% recovered); and (vi) 7,7-difluoronorcarane (15) (0.155 g, 1.18 mmol, 47%).

(iv) Flow pyrolysis. The cyclopropane (6) (3.64 g, 20.0 mmol), passed *in vacuo* at low pressure (1–2 mmHg) through a silica tube (55 cm, 8 cm internal diameter) heated at 375 °C (contact time 2.31 s), gave (i) carbon monoxide (trace); (ii) silicon tetrafluoride (trace); (iii) a mixture of tetrafluoroethylene (0.582 g, 5.82 mmol, 58%) and hexafluoropropene (0.031 g, 0.2 mmol, 3%); (iv) octafluorocyclobutane (0.33 g, 1.65 mmol, 33%); and (v) (5) (2.586 g, 19.6 mmol, 98%).

(v) Flow pyrolysis in the presence of cyclohexene. A mixture of the cyclopropane (6) (3.64 g, 20.0 mmol) and cyclohexene (16.40 g, 0.20 mol), pyrolysed as in the previous experiment at 375 °C (contact time 2.35 s), gave (i) tetrafluoroethylene (0.36 g, 3.6 mmol, 36%); (ii) octafluorocyclobutane (0.22 g, 1.1 mmol, 22%); (iii) (5) (2.59 g, 19.6 mmol, 98%); (iv) unchanged cyclohexene (15.10 g, 0.184 mmol, 92% recovered); and (v) (15) (1.085 g, 7.8 mmol, 39%).

(j) 1-Fluoro-1-difluoromethylcyclopropane (7). A sample of the cyclopropane on static pyrolysis at 380 °C (20 h) was recovered unchanged (91%)

[9/058 Received, 12th January, 1979]

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